



RICE UNIVERSITY

Ionization and Dissociation Studies of  
Propadiene, 1,3-Butadiene, 1,3 trans-Pentadiene,  
2,4-Hexadiene and 2,5-Dimethyl-2,4-Hexadiene  
by Electron Impact

by

Al Mogenis

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Thesis Director's signature:

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## ABSTRACT

Ionization and Dissociation Studies of  
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The ionization and dissociation of propadiene, 1,3-butadiene, 1,3-trans-pentadiene, 2,4-hexadiene and 2,5-dimethyl-2,4-hexadiene have been studied using a CEC-21-701 mass spectrometer. The ionization potentials measured show good agreement to that reported previously by other workers. For 2,4-hexadiene and 2,5-dimethyl-hexadiene, whose appearance potentials have not been measured before, the results are in close agreement with the calculated values of their ionization potentials using the group orbital method. The appearance potentials of the principal ions from these compounds were measured and heats of formation of the ions were calculated when a reaction mechanism could be assigned. For processes where more than one reaction path was possible, the mechanism assigned was on the basis of the evidence of metastable ion transitions that could be correlated to the reaction in question. By a comparison of the heat of formation of ions produced from different sources, it is sometimes possible to decide whether excess energy is required for its formation from the alkadiene under examination.

## ACKNOWLEDGMENTS

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## TABLE OF CONTENTS

ACKNOWLEDGMENTS - - - - -	ii
LIST OF TABLES - - - - -	iv
LIST OF FIGURES - - - - -	v
INTRODUCTION - - - - -	1
DETERMINATION OF APPEARANCE POTENTIALS - - - - -	3
A. Standard Techniques of Ionization Efficiency	
Curve Analysis - - - - -	6
B. Thermochemical Considerations - - - - -	9
APPARATUS AND EXPERIMENTAL - - - - -	15
Apparatus - - - - -	15
Modifications - - - - -	18
Analyzer Assembly - - - - -	18
Pumping System - - - - -	19
Electronics - - - - -	21
Recording System - - - - -	23
Inlet Systems - - - - -	23
Experimental Technique - - - - -	28
Materials - - - - -	29
RESULTS AND DISCUSSION - - - - -	30
Ionization Potentials - - - - -	30
Appearance Potentials - - - - -	32
Propadiene - - - - -	32
1,3-Butadiene - - - - -	33
1,3- <u>trans</u> -Pentadiene - - - - -	37
2,4-Hexadiene - - - - -	41
2,5-Dimethyl-2,4-Hexadiene - - - - -	43
Mass Spectra - - - - -	45
CONCLUSION - - - - -	46
BIBLIOGRAPHY - - - - -	48

# LIST OF TABLES

Table 1.	Ionization Potentials - - - - -	51
Table 2.	Appearance Potentials - Propadiene - - - - -	52
Table 3.	Appearance Potentials - 1,3-Butadiene - - - - -	53
Table 4.	Appearance Potentials - 1,3- <u>trans</u> -Pentadiene - - -	54
Table 5.	Appearance Potentials - 2,4-Hexadiene - - - - -	55
Table 6.	Appearance Potentials - 2,5-Dimethyl-2,4-Hexadiene -	56
Table 7.	Mass Spectrum @ 50v - Propadiene - - - - -	57
Table 8.	Mass Spectrum @ 50v - 1,3-Butadiene - - - - -	58
Table 9.	Mass Spectrum @ 50v - 1,3 <u>trans</u> -Pentadiene - - - - -	60
Table 10.	Mass Spectrum @ 50v - 2,4-Hexadiene - - - - -	62
Table 11.	Mass Spectrum @ 50v - 2,5-Dimethyl-2,4-Hexadiene - -	64

# LIST OF FIGURES

	<u>Page</u>
Figure 1. Typical Ionization Efficiency Curves for an Ion of High Intensity ( $C_5H_8^+$ ) and That for an Ion of Low Intensity ( $C_3H_2^+$ ) from 1,3- <u>trans</u> -Pentadiene. - - - - -	4
Figure 2. Typical Ionization Efficiency Curve for a Doubly Charged Ion - - - - -	5
Figure 3. Illustration of the Linear Extrapolation Method and the Semi-Log Methods - - - - -	8
Figure 4. Illustration of the Extrapolated Voltage Difference Method - - - - -	-10
Figure 5. Franck-Condon Principle for a Diatomic Molecule $R_1R_2$ Showing the Difference between Vertical and Adiabatic Transitions - - - - -	13
Figure 6. Diagram of the Analyzer of the CEC-21-701 Mass Spectrometer. The magnetic field is directed out of the plane of the paper and the electric field is directed radially outward. - - - - -	16
Figure 7. Schematic of the Isatron 21-103C Source Used in the CEC 21-701 Mass Spectrometer - - - - -	20
Figure 8. Schematic of Field Plate Voltage Balance Monitor Circuit -	24
Figure 9. Simplified Diagram of Heated Inlet System - - - - -	25
Figure 10. Diagram of Caton Ultra High Vacuum Coupling Showing Method of Leak Mounting Between Two Aluminum Gaskets - -	27

## INTRODUCTION

The study of ions produced by electron impact upon gases can produce much information about a particular process involved. Through an analysis of an ionization efficiency curve (ion current vs. electron energy) it is possible to determine the energy necessary for the production of an ion from a given compound. The measured appearance potential of an ion can be treated as the thermodynamic function  $\Delta H$  reaction, if the products, ion and neutrals are formed with no excess energy. In the case where excess (excitational) energy is required the appearance potential is then a measure of the energy required for that process alone, with the products being formed in their particular excited states (vibrational, electronic, rotational or translational). By a comparison of the heat of formation of an ion from different sources it is sometimes possible to assign a reaction path in a particular case where there is more than one choice possible and decide whether any excess energy is involved in its formation.

This work concerns itself with the measurement of the appearance potentials of principal ions produced by electron impact on propadiene, 1,3-butadiene, 1,3 trans-pentadiene, 2,4-hexadiene and 2,5-dimethyl-2,4-hexadiene. The alkadienes in general have not been extensively examined from the viewpoint of ionization and dissociation by electron impact. The ionization potentials of propadiene (49, 7, 10), 1,3-butadiene (7,35,56) and 1,3 trans-pentadiene (8,) have been previously determined. With the exception of the  $C_3H_3^+$  and  $C_3H_2^+$  ions

whose appearance potentials from propadiene and 1,3-butadiene were previously determined (7) no other ions seem to have been studied from these compounds. This study reports the appearance potentials of the principal ions from these compounds and their calculated heats of formation whenever a definite reaction path can be assigned.

A convenient method for acquiring appearance potential data is through the use of a mass spectrometer. This has the advantage that it produces ions and also separates them according to their mass/charge ratios. In this manner it is possible to study one particular kind of ion, though several may be formed simultaneously. The instrument used in this study was a Consolidated Electrodynamics Corporation (CEC) 21-701 mass spectrometer which was extensively modified before data could be taken.

## DETERMINATION OF APPEARANCE POTENTIALS

A typical ionization curve obtained in the course of this investigation is shown in Figure 1a. It was obtained by monitoring the ion current (sweeping repeatedly over the mass) while varying the electron energy in small increments. It exhibits the typical characteristics of ionization efficiency curves as described by previous investigators (23). The linear portion terminates with a curved portion for a volt or so above the threshold voltage. For comparison the ionization efficiency curve for a fragment ion from the same compound is given in Figure 1b. The fragment ion curve shows considerably more curvature, a characteristic of ions of low intensity. Since the magnitude of the electron flux, collector efficiency and the sample pressure are not known with any degree of certainty, an arbitrary ion current scale is usually selected. It is convenient to measure the ion intensity at 50 or 70 eV and, setting this value to be 100%, refer other ion currents to it. For doubly charged ions a plot of the square root of the ion intensity against electron energy was found to give a more satisfactory ionization efficiency curve in agreement with Morrison et al. (36). A typical plot for a doubly charged ion is shown in Figure 2.

Since the ionizing electrons receive energy from sources other than the potentials applied between the filament and the block, the electron energy scale must be calibrated. This can be accomplished by determining the ionization efficiency curve of a substance whose ionization potential is accurately known at the same time that the

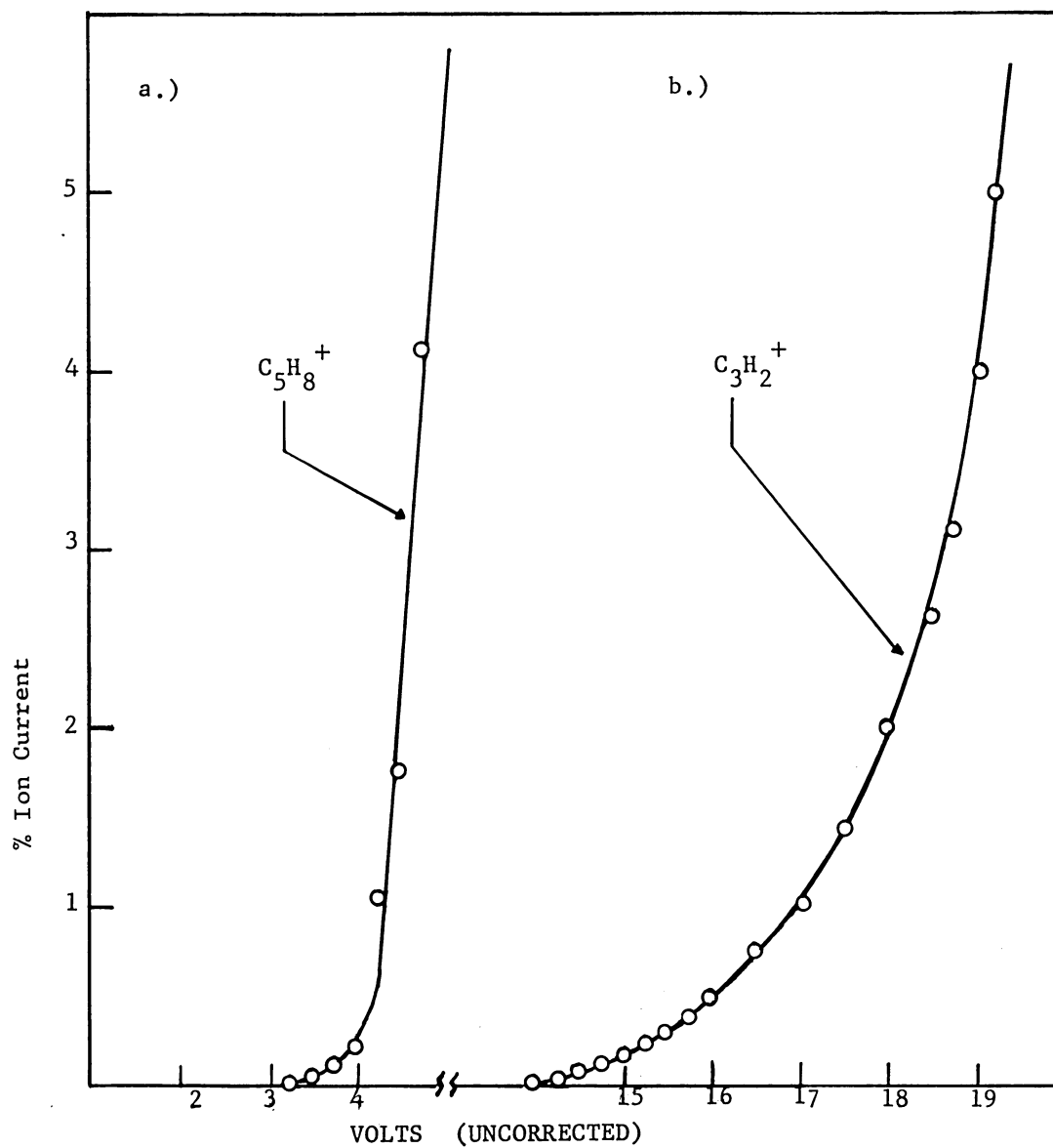


FIGURE I

Typical Ionization Efficiency Curves for an Ion of High Intensity ( $C_5H_8^+$ ) and that for an Ion of Low Intensity ( $C_3H_2^+$ ) from 1,3-trans-Pentadiene

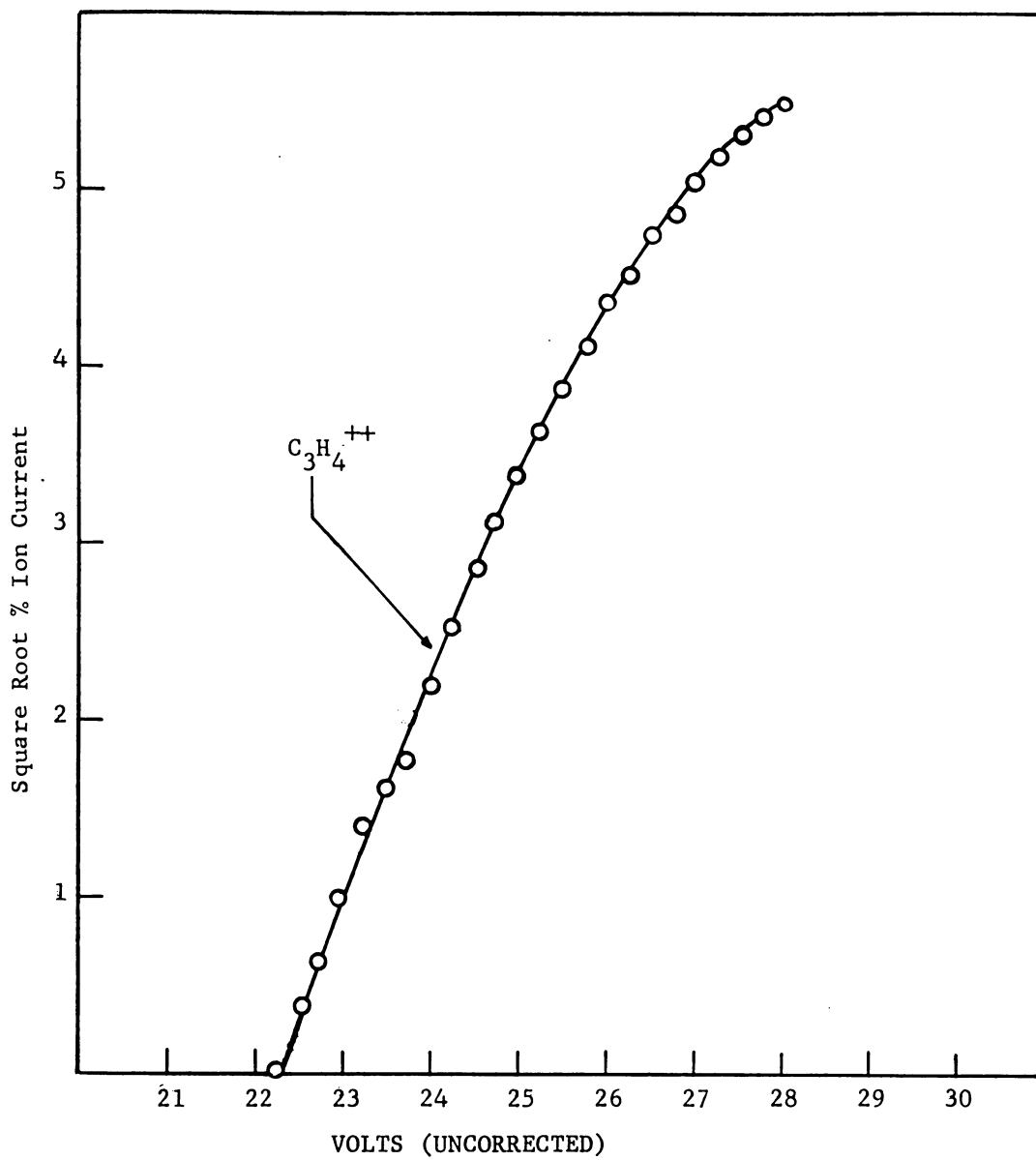


FIGURE 2  
Typical Ionization Efficiency Curve for a Doubly Charged Ion

sample is present. In this technique the voltage scale is set by the reference and the sample ionization efficiency curves are referred to this known curve. It is usually found that a constant voltage may be added to the measured value to yield a satisfactorily accurate value for the appearance potential. Usually one of the inert gases are used, since their ionization potentials have been determined accurately by spectroscopic means.

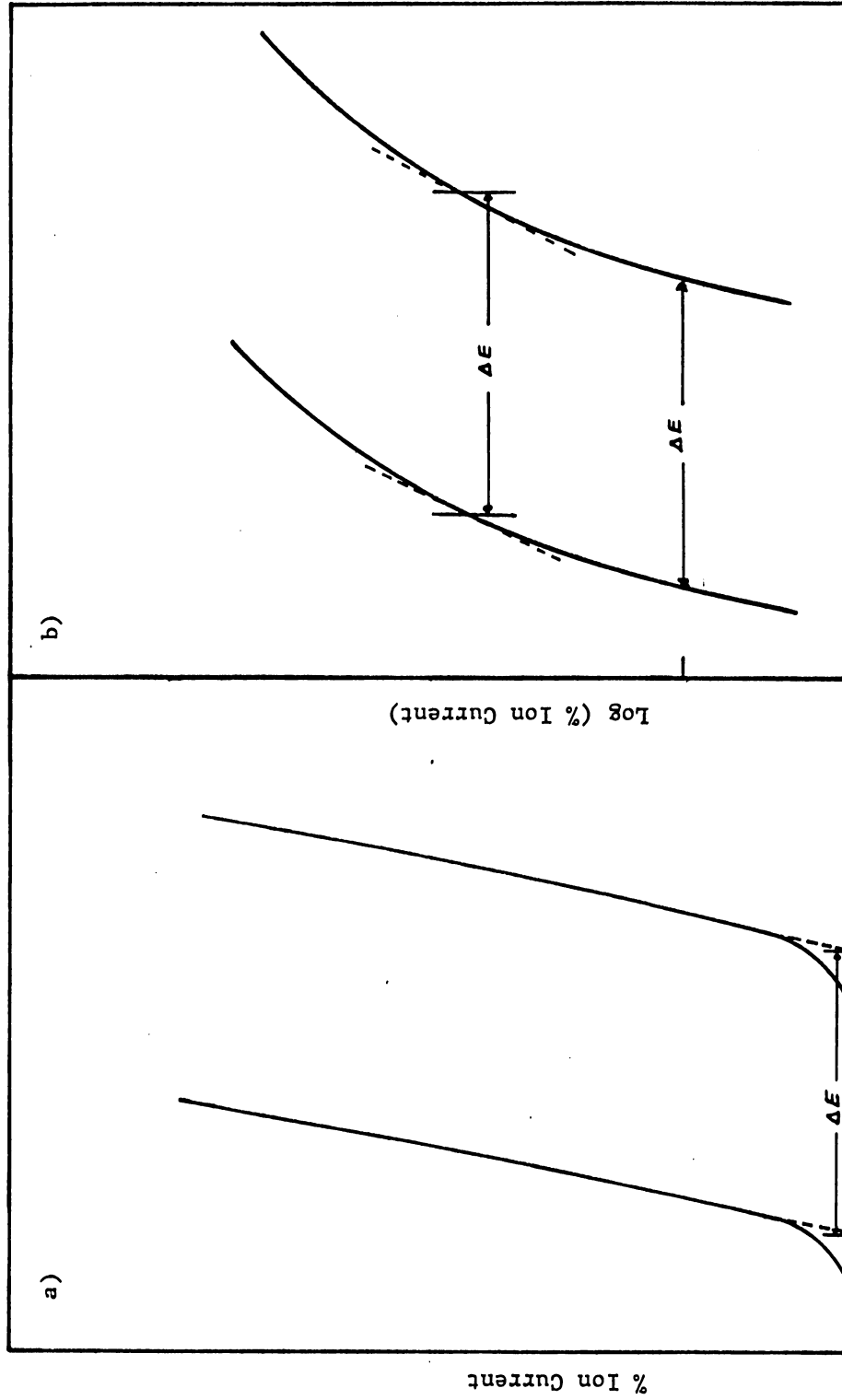
A. Standard Techniques of Ionization Efficiency Curve Analysis.

Several techniques are used for analyzing ionization efficiency curves. All of these methods are of an empirical nature and rely on graphical methods of solution. The first method that appears to have been used (47) is called the vanishing current or initial onset. This simply involves the determination of the point where the curve intersects the energy axis. It is perhaps the simplest in its approach but practically it is found to be prone to subjective error since the curve approaches the energy axis asymptotically. Some workers have rejected this method arguing that because of the exponential nature of the decrease in ion current, it never reaches zero, but many others have found it to be quite satisfactory judging from the results they have obtained by careful use of the vanishing current method (14).

The linear extrapolation method (52) determines the threshold voltage by extrapolating the rising linear portion of the ionization efficiency curve to zero ionic current. This method does away with the ambiguity of fixing the critical potential but in practise has

been found to give consistently high results. One other difficulty arises when the ion exhibits an ionization curve such as in Figure 1b, where the extrapolation of the linear portion is somewhat arbitrary. An illustration of this method appears in Figure 3a.

Two methods employ the semi-log plot of the percent-ion current versus electron energy. Honig's critical slope method (23) determines the slope of the linear portion of the semi-log plot and then the point on the curve whose tangent is  $2/3$  this value. The difference in electron energy between these two points of the reference and sample are taken as the difference in appearance potentials of the ions (see Figure 3). Though the soundness of the derivation of this method has been questioned (14,27,45) it must be admitted that it has been capable of some very good results. The other method utilizing a semi-log plot is that due to Lossing et al. (31). It is found that when a semi-logarithmic plot of ion current as a function of electron energy is prepared, the curve for the calibrant and the sample approach linearity and are parallel below about 3% of ion intensity. The difference in electron energy at 1% is taken to be the difference between the appearance potentials of the calibrant and unknown ions (Figure 3b). A quick method requiring no graphical display, based on the semi-log technique is known as the energy compensating technique (26). It consists of measuring the ion currents of the calibrant and unknown ions at 50 v and then determining the energies at which each of the ions currents are 1% of their 50 v values. The difference in the 1% values is taken as the difference in the appearance potentials. This method has its advantages in that it only takes



Electron Energy

FIGURE 3

Illustration of the Linear Extrapolation Method and the Semi-Log Methods

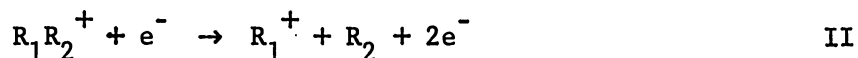
seconds to do, but it gives only approximate results. A method which is similar to the vanishing current one, but somewhat less subjective than the former, is that due to Warren (58). Adjusted to the same intensities at 50 v, the linear portions of the ionization efficiency curves are forced parallel and the difference in the electron energy between the ion of interest and the calibrant is plotted as a function of ion current. Usually a plot from 5% to 0.5% ion current is sufficient for an extrapolation to zero ion current. This intercept on the energy axis is taken as the difference in the ionization potentials of the two ions (see Figure 4). This method has been adopted in analyzing the data taken in this work. It was found to be quite reproducible. Usually for the parent or other intense ions the reproducibility was  $\pm 0.03$  eV while that for the fragments of lesser intensity reproducibility was generally  $\pm 0.1$  eV. These limits represent the average deviation from the mean and can by no means be assumed to be the absolute error of the measurement.

#### B. Thermochemical Considerations.

A molecule undergoing collision with an electron is subject to a variety of reactions. In the case of alkadienes as with most hydrocarbons the reactions most frequently encountered are



where the parent ion is formed and



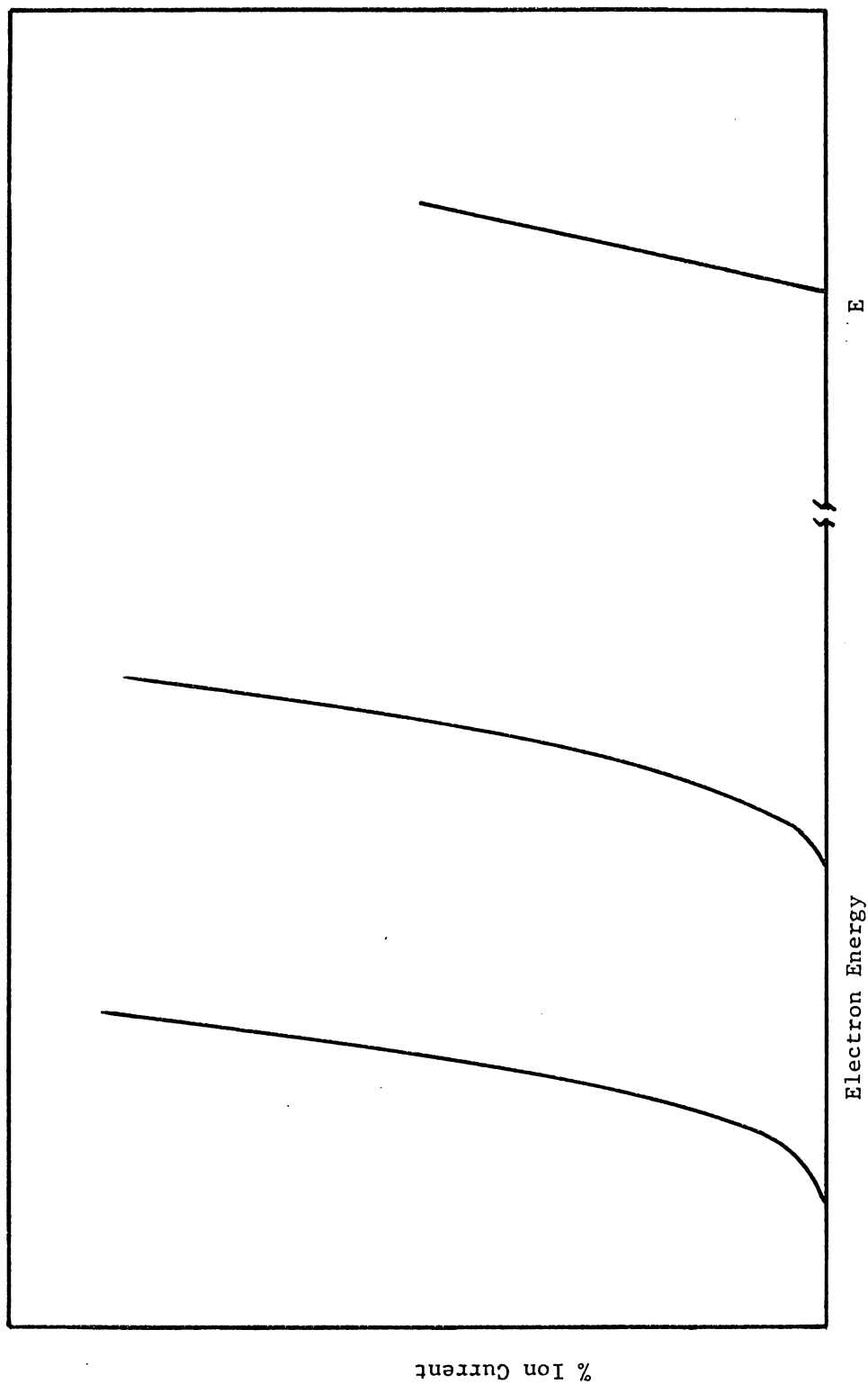


FIGURE 4  
Illustration of the Extrapolated Voltage Difference Method

which describes the formation of the various fragments. Applying the usual methods of thermochemistry we may write for (II).

$$\Delta H_{\text{reaction}} = \Delta H_f(R_1^+) + \Delta H_f(R_2) - \Delta H_f(R_1R_2) + \text{excess energy} \quad \text{III}$$

Now the appearance potential of an ion may be taken as the heat of reaction necessary to produce that ion from a given compound. If no excess energy is involved we may equate the  $\Delta H_{\text{reaction}}$  with the appearance potential,  $A(R_1^+)$ , and, where heats of formation of two of the participants are known, the other may be calculated. An alternate and frequently encountered equivalent expression for (III) is

$$A(R_1^+) = I(R_1) + D(R_1 - R_2) \quad \text{IV}$$

That this is true may be readily seen from the fact that by definition  $I(R_1) = \Delta H_f(R_1^+) - \Delta H_f(R_1)$  and  $D(R_1 - R_2) = \Delta H_f(R_1) + \Delta H_f(R_2) - \Delta H_f(R_1R_2)$ . It should be emphasized that the above equations (III) and (IV) are valid only in cases where no excess (excitational) energy is required.

Appearance potentials determined in this fashion may be those of ions not necessarily in their ground states. However, the relations derived above may still be used as approximations and by a comparison of the heats of formation of ions so determined to the heats of formation of the same ions from different starting materials, reasonable conclusions as to the status of the ion under investigation and its mode of formation can often be deduced.

How ions produced by electron impact may not be in their ground states or require excess energy for their formation may be explained

by considering the potential energy diagram for a simple diatomic molecule (see Figure 5). According to the Franck-Condon principle (9) the internuclear distance of the molecule ionized by an electron does not change during the ionization process. The molecule has the same configuration immediately after the transition as it had immediately before the transition. This means that the transitions that occur are "vertical" ones with the point representing the energy of the molecule before ionization being directly under the point representing the energy of the molecule ion. If the potential energy minima of the molecule and molecule ion are at the same internuclear distance the transition probability would be such that the normal molecule ion in its ground vibrational state will be formed. As the minimum of the potential energy curve of the molecule ion shifts toward greater internuclear separation the transition will occur to higher vibrational states of the molecule-ion and dissociation can occur. If the relation of the two potential energy curves is such that transitions are to those points above the dissociation asymptote or to a repulsive state (no minimum in the potential energy curve) the products of the dissociation would be expected to form with excitational energy. This concept may be extended for polyatomic molecules, with potential energy hypersurfaces to be considered in the same way instead of the easily visualized potential energy curves for diatomic molecules.

Ionization would be expected to occur without any translational energy component being added because of the small mass of the electron compared with the mass of the molecule, but excess vibrational energy may be involved if the Franck-Condon principle does not allow

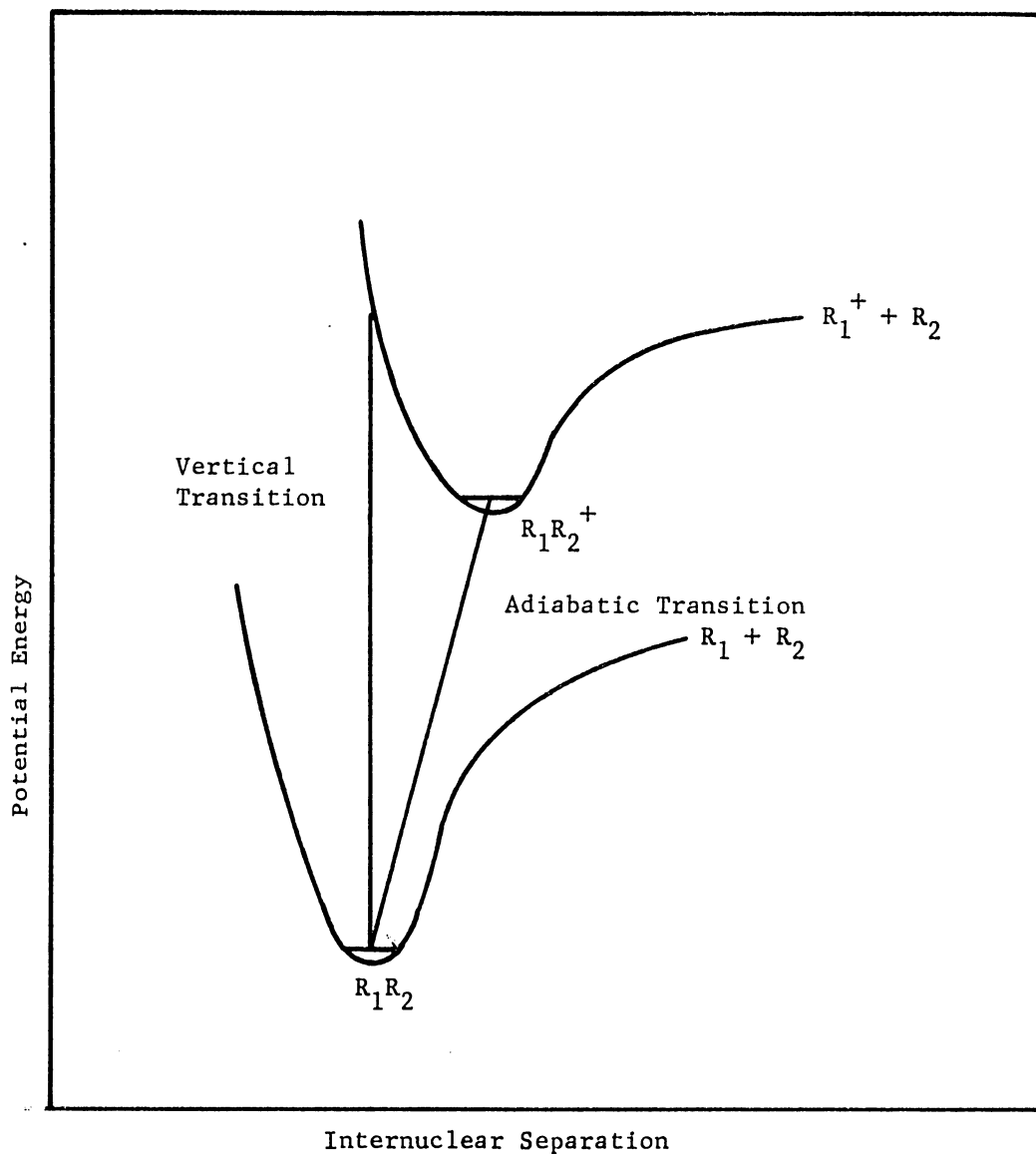


FIGURE 5

Franck-Condon Principle for a Diatomic Molecule  $R_1R_2$  Showing the Difference between Vertical and Adiabatic Transitions

transitions to the ground level in the ionic state. For fragmentation and ionization the distribution of any excess energy that would be involved if the transition is above the dissociation asymptote or to a repulsive state among the various products is hard to predict. Translational energy might be realized in the case of one bond being broken, but for more complex transitions involving simultaneous bond breaking and making, the answer is not so simple. Rotational and vibrational energy have to be considered as possible modes of exhibiting this excess energy also. Prediction of what transitions are most probable for polyatomic molecules is generally impossible because of the lack of information about their various states.

The heats of formation are calculated as being formed at 298°K though the ionization chamber is at a considerably higher temperature. This does not introduce serious error because the heats of formation do not change a great deal with temperature and there is some uncertainty whether the entering gas is equilibrated to the temperature of the source.

## APPARATUS AND EXPERIMENTAL

The CEC-21-701 mass spectrometer was donated by Shell Oil Company and assembled for use in these laboratories. Certain modifications were made on this mass spectrometer to permit measurement of appearance potentials and to increase the flexibility of this instrument. As a consequence of this work a comprehensive manual for the instrument's operation was compiled.

Apparatus: This mass spectrometer was originally constructed in 1957 as a prototype model to see whether a design of coincident sector field double focusing instrument would be of an advantage over other types. The construction and theoretical considerations of this design have been previously described (25,51). The positive ion beam is focused by a  $60^\circ$  radial electric sector installed in a  $60^\circ$  magnetic sector of 11.64 inch radius (see Figure 6). One consequence of this design is that the conjugate focal planes lie nearer to the sector (39) than in a single focusing magnetic instrument. This of course leads to a more compact design of the mass spectrometer. Some disadvantages of this design are the stronger magnetic field that is required because of the increase in the magnet gap to accommodate the field plates and the difficulty of alignment of the instrument due to the fringing effects of the magnetic field. The resolution routinely obtainable during this work was the ability to completely resolve 1 mass unit at mass 1000. This is not optimum for the instrument but was found to be more than adequate for determining appearance potentials of the masses which were generally under 100.

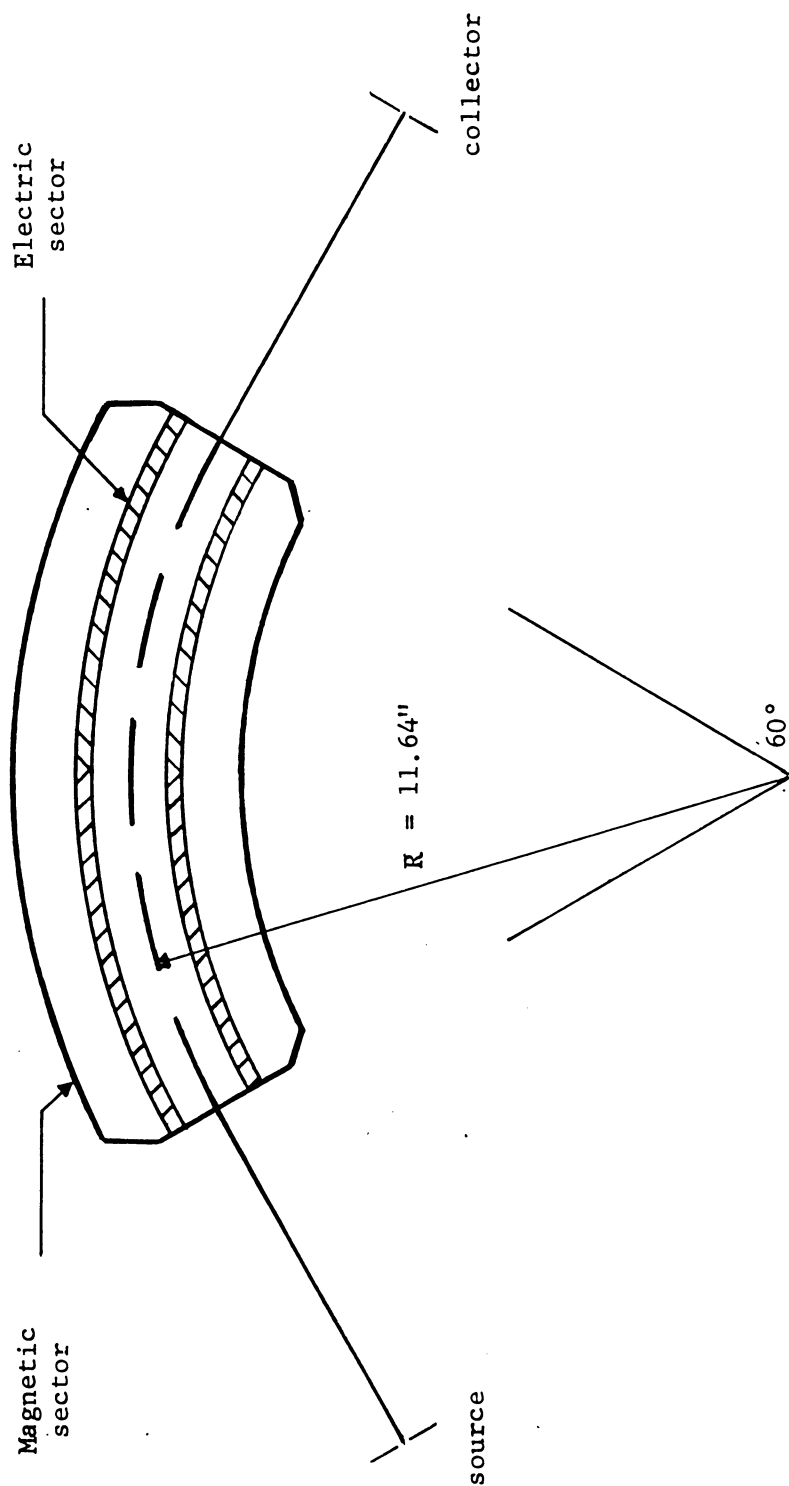


FIGURE 6

Diagram of the Analyzer of the CEC-21-701 Mass Spectrometer  
 The magnetic field is directed out of the plane of the paper and the  
 electric field is directed radially outward.

The basic operation of this instrument may be outlined here. The electrons emitted from an incandescent 6 mil rhenium wire filament are accelerated by a potential difference, variable between 0 and 100 volts, between the filament and the ionization chamber. The electron beam is collimated by passing through an aperture of 1 x 4 mm and held in a tight bundle by an externally adjusted magnetic field. The electron beam is collected on the anode which is kept at 150 v. positive with respect to the ionization chamber. The anode current formed in this manner is typically in the order of several microamperes. The sample to be analyzed is admitted in the gaseous state perpendicular to the electron beam where a portion of the molecules are ionized. The ions formed by electron impact are impelled out of the source by the repeller plates which are usually held at about one volt above the potential of the ionization chamber. The ionization chamber is at the ion accelerating voltage. Having passed out of the source through the first exit slit, the ion beam is focused by the electrostatic lens and accelerated to the second slit which is at ground potential. The ions are accelerated according to their charge and enter the analyzer where they are separated according to their charge/mass ratio. They then pass through the exit slit and strike the collector cathode of the electron multiplier causing secondary electrons to be emitted from the first dynode. These are accelerated toward the second dynode, etc., until the primary electrons are multiplied about  $10^6$  times. These electrons are collected on the anode of the electron multiplier and the resulting DC signal is superimposed on a vibrating reed condenser.

The modified AC signal is amplified and rectified by an electrometer and is conveniently read on a meter or recorded on photographic paper for analysis. Mass selection is accomplished by changing the accelerating voltage while keeping the magnetic field constant. The field plate voltage also changes with the accelerating potential, because to realize focus conditions in this instrument, the field plate voltages have to be a constant fraction of the accelerating potential.

Modifications: The equipment relating to this mass spectrometer may be arbitrarily divided into five areas.

- 1.) The analyzer assembly, consisting of the source chamber, the analyzer tube, the detector housing and the electro magnet.
- 2.) The pumping system, composed of a mechanical roughing pump, diffusion pumps, cold traps and pressure readout gauges.
- 3.) Electronics, containing the various power supplies needed for the operation of the mass spectrometer and circuits for this power distribution.
- 4.) The recording system of the signal made up from an electrometer and a recorder.
- 5.) The inlet system through which the samples can be introduced into the mass spectrometer.

Modifications were made in all of these areas of the instrument to make it suitable for appearance potential work and general mass spectrometer duties.

Analyzer Assembly: The analyzer assembly was dismantled and the internal components that were suspected of causing the deterioration of the quality of signal were examined. It was found that the field plates

were out of alignment and the source in need of cleaning. The field plates were removed and their inner surfaces polished to insure no surface charge effects which have been noted previously as being very profound in affecting the total defocusing of the instrument. The source (see Figure 7 ) was dismantled and polished to remove the carbonaceous deposits. All of the sapphire insulators were replaced with new ones to reduce high voltage leaking across them and the source was reassembled. The electron multiplier was replaced with a 14 stage shielded electron multiplier with Ag-Mg dynodes having a gain of  $10^6$  at an applied voltage of 250 volts across each dynode. This particular multiplier with internal resistors is available only from National Co., Inc.. The lead wires to the multiplier were shortened when it was found that their vibration caused an extraneous signal to be produced. The analyzer tube was carefully reassembled with the field plates realigned and the lead in wires to them suitably insulated by teflon spacers to prevent shorting to the housing. The source housing was modified to accept a standard flange to its inlet port. This eliminated the steel-glass ball joint which was found in practice to be prone to leakage. Before reassembly all of the gaskets were replaced with those made of teflon.

Pumping System: The pumping system did not require extensive modification. The instrument is equipped with a Welch 1405-B two stage rotary pump capable of 0.1 micron pressure. The analyzer and source regions are pumped separately by two glass mercury diffusion pumps, CVC type GHG-15-01. They are of the three stage variety capable of pumping speeds of 19 liters/sec.

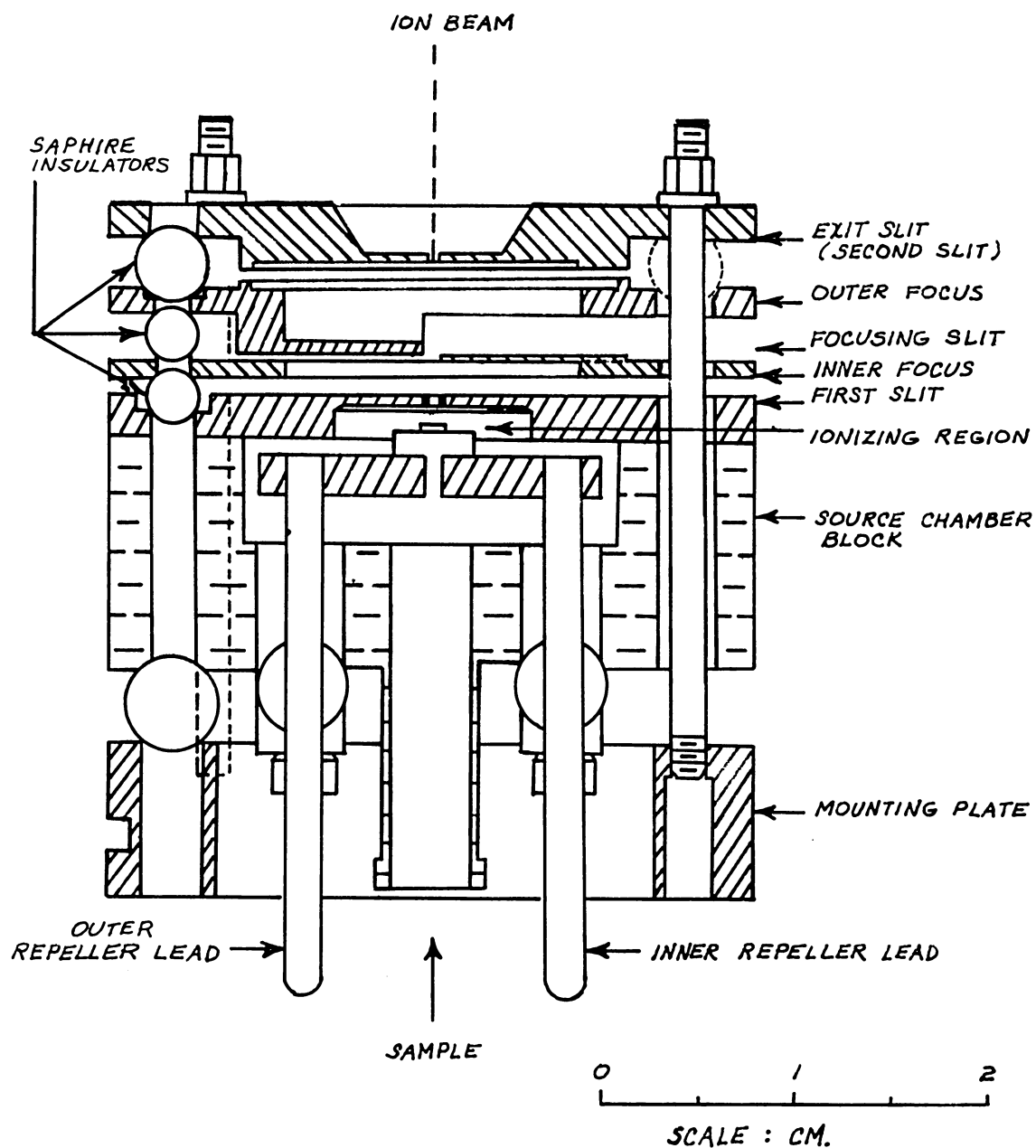


FIGURE 7

Schematic of the Isatron 21-103C Source Used in the  
CEC 21-701 Mass Spectrometer

This speed is enhanced by the cryogenic pumping of the two liquid nitrogen traps which are used in conjunction with these pumps. Though no change was made, it is recommended that pumps of significantly higher speed ( $\sim 750$  liters/sec) be installed in order to prevent backstreaming of the sample and rendering the instrument inoperable. This has been especially true when using Xenon gas whose freezing temperature is not much higher than the boiling point of liquid nitrogen, with the result that the diffusion pumps are not able to remove what the traps are not able to freeze out. If a change of pumps were to be made these traps could also be eliminated and economically replaced by baffles cooled by a conventional refrigeration unit (e.g. CVC PMCS-4B polyphenyl ether pump with a baffle CVC type BCN, in the author's opinion, would make an excellent choice). A Veeco RG-31X vacuum gauge controller using the conventional Bayard-Alpert ionization gauges was installed. This unit has a provision built in whereby it can control a relay in the event of a vacuum failure. A protection circuit was designed where the filament and the diffusion pumps were automatically turned off in case of vacuum failure (i.e.,  $P > 10^{-4}$  mm of Hg). The pumping system thus constructed is capable of keeping the analyzer region at  $2 \times 10^{-7}$  mm of Hg. The source is usually higher due to the introduction of the sample; i.e., about  $8 \times 10^{-7}$  mm of Hg, as measured by the source chamber ionization gauge.

#### Electronics:

The electronic section was modified extensively. Preliminary investigation disclosed that much of the wiring had deteriorated and needed replacing. The instrument was rewired with wire of proper gauge and insulation. Two power supplies were found to be defective;

they were the magnet power supply and the accelerating voltage supply. Repair was ruled out because of their age and a history of erratic performance. The magnet current supply was replaced by a Kepco HB 525 current regulated supply capable of 200 milliamperes at 600 volts. This unit was found in practice to be much superior in maintaining a constant magnetic field due to the superior current regulation of the new circuit. A Harrison 6525A high voltage power supply capable of 4,000 volts at 50 milliamperes was used to replace the original accelerating voltage power supply. The scan programming was not interchangeable and had to be constructed for this new high voltage unit. This was accomplished by driving a 40 turn helical potentiometer by a synchronous electrical motor. The rate of scan was controlled by a continuous ratio reducer, Metron 3-B, and a very smooth and slow scan can be produced. The maximum scan range is 1,000 volts, while the rate can be varied over this interval from 3 to 20 minutes. The emission regulator (source control) was previously modified (38) to permit ionization efficiency curve determination. This was accomplished by setting the repeller voltage by a battery at a fixed 1 volt potential above that of the block of the source. Further modification was made on the repeller voltage control by installing a 10 turn helical potentiometer across a battery and making the repeller voltage variable from 0 to 22 volts. Part of a circuit which was originally on the emission regulator was relocated on a different panel. This relocated focusing panel allowed a quicker check out of its components when aligning the instrument. The field plate voltage balance was monitored by a sensitive

microammeter utilizing a bridge circuit whose schematic is shown in Figure 8. The ionizing voltage is read out from a Leed and Northrup No. 7655 potentiometer, suitably insulated, since the measurement is, in effect, across the filament and block which are at accelerating voltage. Voltage could be measured in 0.1 volt increments with 1% precision.

Recording System: The recording system for the signal for this mass spectrometer consists of an Applied Physics Model 30L vibrating reed electrometer and a CEC type 5-104 recording oscillograph. This system is capable of detecting very small signals, because the electrometer is capable of very small current measurement (ca.  $10^{-15}$  amperes). The recorder's optical system was realigned to produce a better "print" of the signal on the photographic paper (Kodak linagraph type 809) and a mass marking light source installed. This recording oscillograph displays five simultaneous traces of the signal attenuated X1, X3, X10, X30 and X100. The most sensitive trace (X1) which had been cut out was made operable because of the significant improvement of the signal to noise ratio by the installation of the new electron multiplier and tuning of the electrometer. The recorder had to be partially rewired in order to make it compatible with the new scanning control.

Inlet Systems: Two inlet systems were designed and built replacing the gallium fritted disc inlet that came originally with this instrument. The first to be constructed was an all stainless steel inlet capable of handling liquids and solids since it can be heated to 250°C (see Figure 9). Liquid samples (e.g., 1,3 trans-pentadiene, 2,4 hexadiene

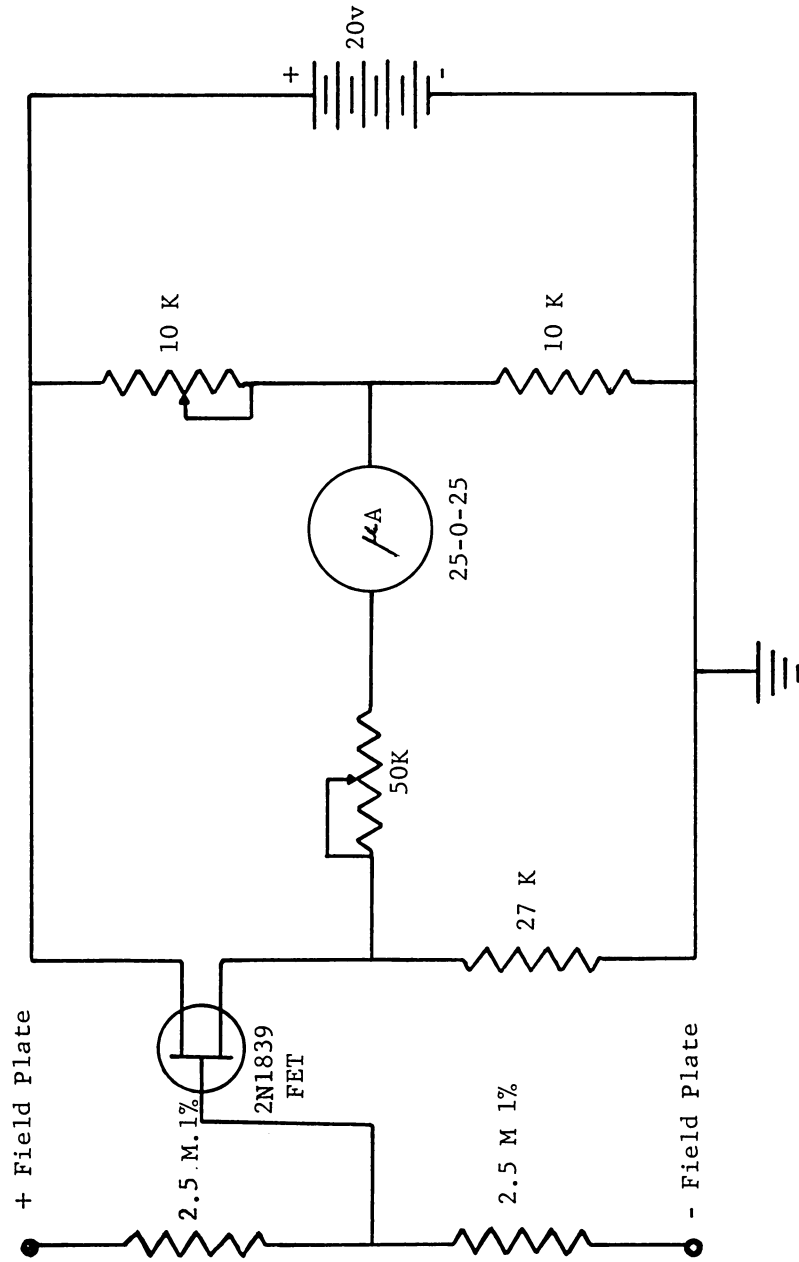


FIGURE 8

Schematic of Field Plate Voltage Balance Monitor Circuit

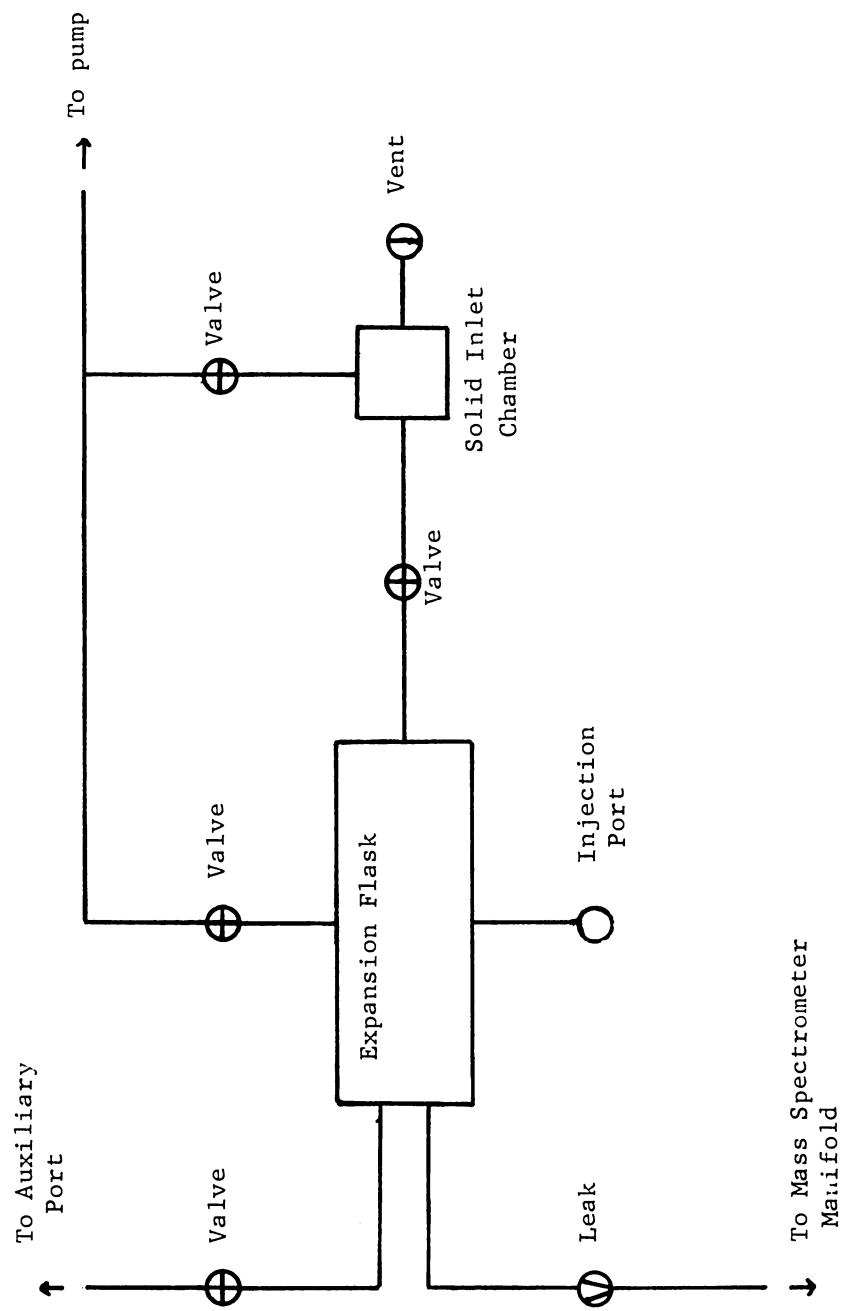


FIGURE 9  
Simplified Diagram of Heated Inlet System

and 2,5-dimethyl-2,4-hexadiene) are injected into the reservoir flask by the use of a gas tight hypodermic syringe through a silicone rubber septum capable of sustaining elevated temperatures. Solids may be introduced into the reservoir through the use of a specially designed vacuum lock. This chamber may be isolated from the rest of the system and vented. Access is gained by removing a blind flange sealer with a neoprene "O" ring. The sample is placed in a small platinum crucible which fits inside a depression in the chamber to insure rapid heat conduction. The chamber is sealed, evacuated, opened to the reservoir and slowly heated until sufficient pressure is produced for analysis. Though none of the samples reported here were introduced in this fashion, the author has had success in obtaining good results with solids whose melting points were as high as 200°C. The valves in this system, as well as on the inlet manifold, are Nupro series "H" bellow valves, capable of sustaining temperatures in excess of 350°C. This inlet system is connected to the manifold of the mass spectrometer via a gold foil leak mounted in a Cajon Ultra High Vacuum Coupling (see Figure 10). We have found very good results in this laboratory using gold foil leaks mounted in this fashion with a considerable savings over the commercially available variety. All of the original glass inlet lines were replaced with 1/4" stainless steel tubing capable of being heated so that no condensation of the sample could occur inside. The other system was unheated and was used for the introduction of gases (e.g., propadiene and 1,3 butadiene). It is of the standard design, consisting of several large glass reservoirs, used for mixing or storing gas samples, and is connected to the inlet manifold by a CEC glass encapsuled

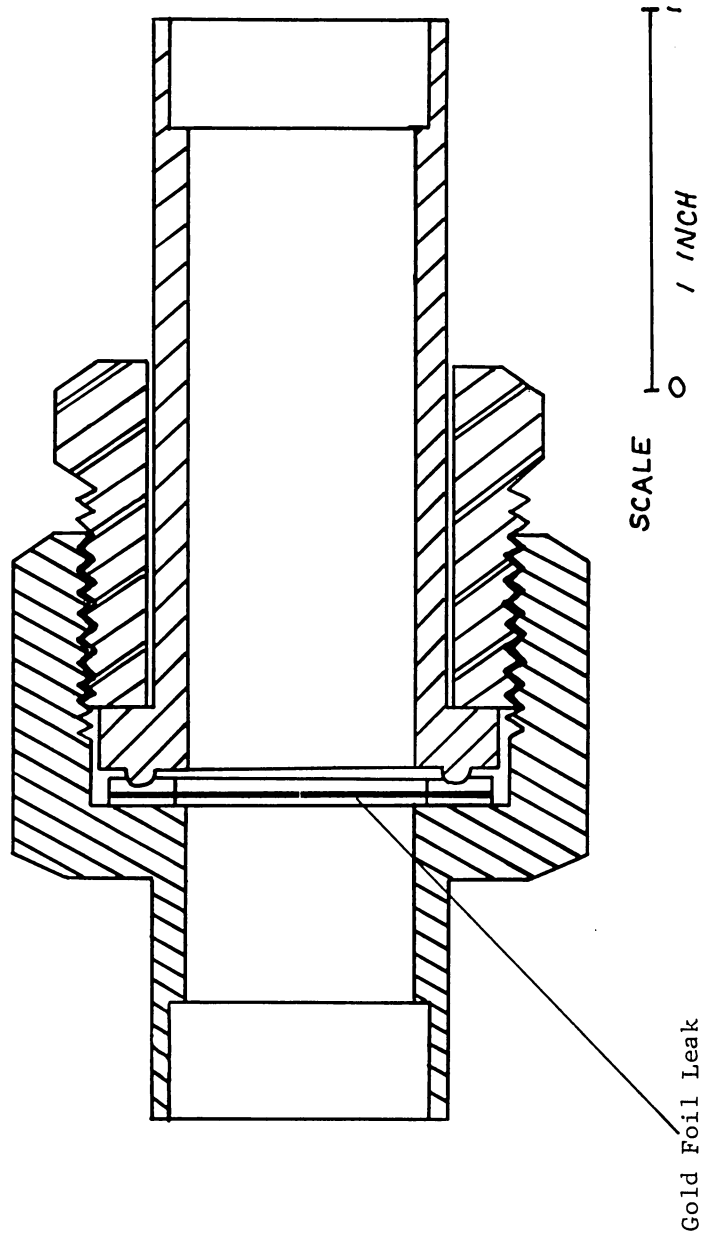


FIGURE 10  
Diagram of Caton Ultra High Vacuum Coupling Showing Method  
of Leak Mounting Between Two Aluminum Gaskets

gold foil leak. These two inlet systems have their own independent pumping systems capable of maintaining the interior at  $10^{-6}$  mm of Hg. The pressure is monitored in these inlets by thermocouple vacuum gauges. The temperature in the heated inlet and along the inlet lines is measured by iron-constantin thermocouples.

Experimental Technique: The procedure for determining ionization efficiency curves was standardized to be as follows. The sample and the calibrating gas were introduced into the inlet system. Their respective pressures were adjusted until their ion intensities were within 10-20% of each other. The manifold valve was then adjusted until the source ionization gauge read  $7 \times 10^{-5}$  mm pressure. The intensity of the calibrant ion and that of the parent ion under investigation are determined at 50 volts (nominal) electron energy. This is accomplished by taking five scans at the same electron energy over the particular ion and averaged. The electron energy is reduced while monitoring the ion intensity until it is about 25% of its 50 volt value. From this point the electron energy is decreased by 1/4 volt increment and the ion intensity recorded for each voltage. This is repeated until no more ion current can be detected on the ion current monitor. The process is repeated twice more for both ions, giving a total of three separate determinations. Having effectively calibrated the energy scale in this manner and determined the ionization efficiency curve of the parent ion, the mixture was pumped out and the sample, by itself, re-introduced into the mass spectrometer to a pressure of  $7 \times 10^{-7}$  mm. The procedure is repeated once again, except that the ionization efficiency curves of the fragment ions are now referred to the parent ion curve instead of the calibrant gas. During all of

these determinations the trap current was kept at 3  $\mu$ amperes. The source temperature was at 250°C as read from a copper-constantin thermocouple. The heated inlet and the inlet lines were kept at 100°C for all of the determinations.

Materials: Propadiene and 1,3-butadiene were obtained from Matheson Scientific Co. The 1,3 trans-pentadiene, 2,4-hexadiene and 2,5 dimethyl-2,4-hexadiene were prepared by Professor Michael Szwarc of State University College of Forestry at Syracuse University.

## RESULTS AND DISCUSSION

The experimental results for propadiene, 1,3-butadiene, 1,3-trans-pentadiene, 2,4-hexadiene and 2,5-dimethyl-2,4-hexadiene are summarized in Tables 1-11. The ionization potentials of these compounds are listed in Table 1. Literature values are included for comparison when such data are available. Tables 2-6 present the appearance potentials and relative abundances of the ions studied in this work. Ionization mechanisms are also indicated by giving in column 3 the neutral products of fragmentation. Heats of formation of ions are calculated on the basis of these mechanisms and literature values for the heats of formation of the various ions are included for comparison with the derived value.

Mass spectral data for these compounds are tabulated in Tables 7-11. The spectra of propadiene, 1,3-butadiene and 1,3-trans-pentadiene obtained in this study are compared with previously reported data. The mass spectra of 2,4-hexadiene and 2,5-dimethyl-2,5-hexadiene have not, to the author's knowledge, been reported, but a comparison with the spectra determined by a CEC-21-701 mass spectrometer are included in Tables 10 and 11.

Ionization Potentials: The ionization potentials determined in this work compare well with values reported by different authors as can be judged from the results presented in Table 1. The ionization potential of propadiene has previously been measured by electron impact (6, 10)

and spectroscopically (49). Our value is in good agreement with both of these reported values. The ionization potential of 1,3-butadiene measured in this work compares well with previous determinations (1a, 6, 56). Only one previous measurement of the ionization potential of 1,3 trans-pentadiene has been reported (8). The value obtained from our study seems to confirm this lone observation very well.

No ionization potentials of 2,4-hexadiene and 2,5-dimethyl-2,4-hexadiene are reported so that a direct comparison is lacking with the values obtained here. However, Franklin (17) has shown that the ionization potentials of molecules may be calculated by the method of group orbitals originally developed by Hall (18a). This method resolves itself into solving the secular equation  $|e_{ij} - E\delta_{ij}| = 0$  where the  $i$  and  $j$  refer to the various groups in the molecule. These groups may, within limits be selected arbitrarily. The roots of the secular equation represent the ionization potentials of the molecule, the lowest being associated with the ionization potential usually measured. This method has been shown to give quite satisfactory calculated ionization potentials for a number of different types of molecules including the polyolefins. The calculation for 2,4-hexadiene can be done quite readily by considering only the first neighbor interactions between the groups chosen as  $\text{CH}_3$ - and  $-\text{HC}=\text{CH}-\text{CH}=\text{CH}-$ . The interaction between the  $\text{CH}_3$ - and diene groups can be readily found since the ionization potential of methane (13.1eV), 1,3-pentadiene (8.7 eV) and 1,3-butadiene (9.1eV) are known. The interaction parameter calculates to be 1.35. Evaluation of the determinant for 2,4-hexadiene

yields as the lowest root 8.4 eV, which is slightly lower than the value reported here. Analogous treatment of 2,5-dimethyl-2,4-hexadiene, we calculate for its ionization potential the value 7.8 eV, again slightly lower than our determined value.

The diolefins exhibit a decrease of ionization potential with increasing number of groups in the molecule. This effect has been previously noted (17) for other homologous series with the magnitude of the effect dependent on the type of compounds. The alkadienes show a smaller change in ionization potential with added methyl groups than do the mono-olefins or the acetylenes.

Appearance Potentials: The appearance potential data are presented in Tables 2-6. The heat of formation of the ion is calculated by the use of the relation,  $\Delta H_f(R^+) = A(R^+) + \Delta H_f(\text{reactant}) - \Delta H_f(\text{Neutral products})$ . The heats of formation for the reactant and neutrals were taken from the latest sources available (1,46,53). For compounds whose heats of formation are not available from the literature, use was made of the Franklin's (16) compiled group equivalents to calculate their  $\Delta H_f$ . The appearance potentials measured in eV are converted to kcal/mole by the identity, 1 eV = 23.06 kcal/mole.

Propadiene: Table 2 presents the results obtained for propadiene. The  $C_3H_4^+$  ion from propadiene appears to be formed in the ground state judging from the spectroscopic value (49) obtained for this compound. The heat of formation of the  $C_3H_4^+$  ion from propadiene closely parallels the values determined from propyne (5) (37) (57) but

reaction  $\text{C}_3\text{H}_3^+ \rightarrow \text{C}_3\text{H}^+ + \text{H}_2$  from the result arrived at by Hipple et al. (21),  $m^* = m^2/m_0$ , where  $m^*$  is the mass of the observed metastable ion,  $m$  the mass of the daughter ion and  $m_0$  the ion undergoing the dissociation. The fact that  $\text{C}_3\text{H}^+$  is formed by loss of  $\text{H}_2$  from  $\text{C}_3\text{H}_3$ , which in turn was formed by loss of H from  $\text{C}_3\text{H}_4^+$  establishes the mechanism.

The doubly charged ions from propadiene whose appearance potentials could be measured are reported here. The calculated heats of formation for  $\text{C}_3\text{H}_4^{++}$ ,  $\text{C}_3\text{H}_3^{++}$  and  $\text{C}_3\text{H}_2^+$  are for the process noted, though for the last mentioned ion, the process might be the loss of 2H instead. It can be seen that the heats of formation for the doubly charged ions are considerably greater than that of their singly charged analogs.

1,3-Butadiene: The results for 1,3-butadiene are summarized in Table 3. The heat of formation of  $\text{C}_4\text{H}_6^+$  compares well with values determined from the same compound and is considerably lower than the  $\text{C}_4\text{H}_6^+$  ion formed from 1,2-butadiene (6), 1-butyne (5,37,56) or 2-butyne (5). Judging from the heat of formation of  $\text{C}_4\text{H}_5^+$  obtained from 1,3-butadiene, the ion is probably not the same as that from either 1 or 2 butyne (5) but intermediate in energy.

The  $\text{C}_4\text{H}_4^+$  ion may be formed either by the loss of  $\text{H}_2$  or 2H. If one assumes the loss of 2H, the calculated heat of formation is unreasonably low in comparison with that from the direct ionization of vinyl acetylene (50). The alternate choice yields a heat of formation for the  $\text{C}_4\text{H}_4^+$  ion which is significantly higher than that observed

is significantly lower than that obtained from cyclopropene (8). The  $C_3H_4^+$  ion from cyclopropene must be cyclic and appears to be less stable than its linear counterpart. The heat of formation of the  $C_3H_3^+$  ion is in good agreement with that determined from the same compound (7) and from several of its isomers (59).

$C_3H_2^+$  may be formed by one of two routes, i.e., by the loss of either  $H_2$  or  $2H$ . The former path is assigned from the following considerations. Examination of a series of radical ions of unsaturated aliphatic hydrocarbons of the general formulae  $C_nH_{2n}^+$ ,  $C_nH_{2n-2}^+$ , etc., reveals a trend of increasing heat of formation with each successive loss of  $H_2$ .  $C_3H_2^+$  may be compared to the series (values of  $\Delta H_f$  taken from Field and Franklin (14))

Ion	$\Delta H_f$ (kcal/mole)
$C_3H_6^+$	229
$C_3H_4^+$	281
$C_3H_2^+$	?
$C_3^+$	480

The  $\Delta H_f$  for  $C_3H_2^+$  calculated for the loss of  $H_2$  is 377 kcal/mole, while only 273 kcal/mole for the loss of  $2H$ . The value obtained for the reaction producing  $H_2$  is more in line with the increasing heats of formation than the alternate choice and must be taken as the more probable representation of the actual process.

The  $C_3H^+$  ionization mechanism is confirmed by the observance of the only metastable transition at mass 35 in the mass spectrum of propadiene (3). This metastable transition may be related to the

from 1-butyne or vinyl acetylene (50). The structure of the  $C_4H_4^+$  from these last two compounds can be the same if the loss of  $H_2$  from 1-butyne occurs from two adjacent carbons yielding  $CH_2=CH-C\equiv CH$  which is ionized. This structure would be expected from the direct ionization of vinyl acetylene. The close agreement of the heats of formation suggests that these ions are the same. This structure, on the other hand, would be hard to attain from 2-butyne and the observed heats of formation (5) suggest that the ion that is formed is of some higher energy structure and probably in an excited state.

The only process that can be reasonably proposed for the production of  $C_4H_3^+$  is the loss of  $H_2 + H$ . If the process  $3H$  is chosen, then the calculated heat of formation is unreasonably low in comparison with what one gets from vinyl acetylene (15). This ion then also seems to be formed in a structure energetically more unstable than that attainable for the same processes from 1 or 2-butyne (5).

The formation of  $C_4H_2^+$  from 1,3 butadiene apparently requires a considerable amount of excess energy. The heat of formation for  $C_4H_2^+$ , calculated for the only process that is energetically reasonable, is considerably higher than that found from diacetylene (5) and from vinylacetylene (15).

The reaction assigned for the production of  $C_3H_3^+$  from this compound is confirmed from the metastable transition observed at mass 28.2 (3). This transition may be correlated to  $C_4H_6^+ \rightarrow C_3H_3^+ + CH_3$ .

The calculated heat of formation is slightly lower than other determinations from this same compound (5,6). The heat of formation of  $C_3H_3^+$  from cyclo- $C_3H_4$  (59) is considerably higher than that of the more stable linear species which is formed here.

The loss of  $C_2H_2$  with the production of  $C_2H_4^+$  from 1,3-butadiene is the only mechanism energetically possible. The resultant value of the heat of formation is slightly higher than that previously reported from ethylene itself. (7,32,54,55). This suggests a slight excess energy required for its formation. The agreement is surprisingly good, considering the complex rearrangement that must have occurred to give these two products.

The metastable transition observed at mass 13.5 can be shown to be the process  $C_4H_6^+ \rightarrow C_2H_3^+ + C_2H_3$ . By calculation of the heat of formation of  $C_2H_3^+$  on the basis of this evidence, we are led to the conclusion that some excess energy is required to cleave this molecule in half.

The formation mechanism of  $C_2H_2^+$  is verified by the metastable transition at mass 28.1 (3). This can be correlated for the reaction  $C_2H_4^+ \rightarrow C_2H_2^+ + H_2$ . Combining this information with the reaction mechanism for the  $C_2H_4^+$  formation, we can calculate the heat of formation for  $C_2H_2^+$ . Comparing the calculated value with that previously reported for the  $C_2H_2^+$  we conclude that considerable excess energy is needed to produce this ion from 1,3-butadiene.

The doubly charged  $C_4H_3^{++}$  appearance potential measurement, coupled with the reaction stated, yields a heat of reaction quite high in comparison with any of the singly charged species from this compound. Somewhat surprisingly, this process requires somewhat more energy than does the similar one for formation of the  $(m-1)^{++}$  ion from allene.

1,3 trans-Pentadiene. The heat of formation of  $C_5H_8^+$  appears to vary with structure as judged from values for various isomers obtained from the literature. Among the pentadienes the 1,3 configuration is of lower energy in both the neutral and ionic states than its isomers.  $C_5H_7^+$  ion appears to be quite similar energetically to that from cyclo- $C_6H_{10}^+$  (22) and of somewhat lower energy than that observed from cyclo- $C_5H_8^+$  (22). However the data in the literature for this ion are very limited so it would be premature to draw any conclusions as to its structure or energy. The mechanism of formation of  $C_5H_6^+$  is assigned from the evidence of the metastable transition observed at mass 64.1 (3), which is  $C_5H_8^+ \rightarrow C_5H_6^+ + H_2$ . The calculated heat of formation is significantly higher than that observed from cyclo- $C_5H_6$  (19). If we assume loss of  $H_2$  from 1,3 trans-pentadiene from two adjacent carbons to form the corresponding alkyne we can estimate its ionization potential by the group orbital method. If the loss of  $H_2$  is from the 3 and 4 carbons, the resulting structure would be  $CH_2 = CH - C \equiv C - CH_3$  whose heat of formation can be estimated using group equivalents as 58 kcal/mole. Calculation of the ionization potential is possible by choosing the groups as  $CH_2=CH-$ ,  $-C \equiv C-$  and  $-CH_3$ .

The corresponding ionization potentials of ethylene (10.5 eV), acetylene (11.4 eV) and methane (13.1 eV) are known. The interaction parameter between the groups  $\text{CH}_2=\text{CH}-$  and  $-\text{C}\equiv\text{C}-$  can be calculated because the ionization potential of vinylacetylene (9.9 eV) (50) has been determined. This interaction parameter is found to be 0.95. The interaction parameter between the groups  $\text{CH}_3-$  and  $-\text{C}\equiv\text{C}-$  is also readily calculated for the ionization potential of propyne (10.3 eV) is known. This turns out to be 3.0. The lowest root for the  $\text{CH}_2=\text{CH}-\text{C}\equiv\text{C}-\text{CH}_3$  determinant, using the above two parameters, is 9.8 eV, which of course corresponds to the ionization potential of this molecule. Combining this value with the calculated heat of formation of the neutral we get 284 kcal/mol as the heat of formation of the linear ion  $\text{C}_5\text{H}_6^+$ . While this is not in exact agreement with the measured value, the agreement is close enough to suggest that the ion we observe is not of a cyclic structure. The cyclic  $\text{C}_5\text{H}_6^+$  is much lower in energy than that possible for the linear structure which is observed in this determination.

The mechanism of formation of  $\text{C}_5\text{H}_5^+$  can be readily established from the two metastable transitions observed at masses 64.1 and 63.1 (3). These processes are  $\text{C}_5\text{H}_8^+ \rightarrow \text{C}_5\text{H}_6^+ + \text{H}_2$  and  $\text{C}_5\text{H}_6^+ \rightarrow \text{C}_5\text{H}_5^+ + \text{H}$  which can be combined to give  $\text{C}_5\text{H}_8^+ \rightarrow \text{C}_5\text{H}_5^+ + \text{H}_2 + \text{H}$ . The calculated heat of formation of  $\text{C}_5\text{H}_5^+$  is slightly higher than that obtained for this ion from cyclo  $\text{C}_5\text{H}_6$  (19) and lower than that from cycloheptatriene (29). The differences are probably due to isomerization energies between the ions that are formed.

The neutral products assigned for  $C_4H_6^+$  and  $C_4H_5^+$  production are the only ones energetically possible. The calculated heat of formation for  $C_4H_6^+$  ion appears surprisingly low in comparison with the value observed from 1,3-butadiene (1a,6,56). No reason can be given for this low value determined here. The  $C_4H_5^+$  heat of formation compared to that from 1,3-butadiene is considerably higher and presumably requires excess energy in its formation.

The formation mechanism of  $C_4H_4^+$  is speculative because the process is not the only one that could be proposed to yield reasonable products, e.g., neutrals could be  $CH + H + H_2$  and  $\Delta H_f$  would calculate to be 312 kcal/mole. The same type of choice is found in the case of the  $C_4H_3^+$  where other processes might be argued to take place. Their heats of formation are admittedly high, and probably are attributable to ionization to a repulsive state several volts above the minimum decomposition asymptote.

Excess energy seems to be involved in the production of the  $C_3H_6^+$  because of the quite high heat of formation value calculated for the only reasonable energetic process. Even if the highly energetic cyclo- $C_3H_6^+$  (55) was formed, considerable energy is still unaccounted for.

The reaction mechanism for  $C_3H_5^+$  formation is quite clear from the metastable observation at mass 25.1 which corresponds to  $C_5H_7^+ \rightarrow C_3H_5^+ + C_2H_2$ .

The calculated heat of formation is higher than that of the linear  $C_3H_5^+$ , strongly suggesting that the  $C_3H_5^+$  formed here might be the cyclic ion or the process requires excess energy.

The products for  $C_3H_4^+$  formation are limited energetically to what is noted. Some excess energy is required for  $C_3H_4^+$  formation, judging from the heats of formation of this ion from linear molecules like propadiene (5) (6) or Propyne(59).

The formation path of  $C_3H_3^+$  is confirmed by the observation of metastable transition at masses 25.1 and 37.1. These transitions are  $C_5H_7^+ \rightarrow C_3H_5^+ + C_2H_2$  and  $C_3H_5^+ \rightarrow C_3H_3^+ + H_2$ , which, when combined, define the mechanisms of the  $C_3H_3^+$  formation as listed. The heat of reaction calculated for this process is in very good agreement with previous reported values for this ion's formation from simpler molecules. This is quite remarkable because of the degree of breaking up and rearrangement of the molecule with no excess energy apparently needed.

No reaction mechanism could be chosen for the production of  $C_3H_2^+$ .

The doubly charged ions whose appearance potentials were measured are tabulated. The heats of formation calculated from the reactions that are assigned show an increase in the heat of formation of the ion with each successive loss of hydrogen. No appearance potentials for these ions have been reported. Any conclusions as to their formation are quite arbitrary.

2,4-Hexadiene: In Table 5 are listed the results for 2,4-hexadiene obtained in this study. The heat of formation of 2,4-hexadiene has not been reported and was calculated to be 17 kcal/mole by the use of group equivalents (16). This value was used for calculating the heats of formation of the ions studied.

The heat of formation of the  $C_6H_{10}^+$  ion appears to be slightly above that formed from cyclohexene (22,35,42,55) which is the only other source that has been reported for this ion. No literature value could be found for the comparison of the heat of formation of the  $C_6H_9^+$  ion. The process for the production of  $C_6H_9^+$  from 2,4-hexadiene is straightforward with a loss of H and the calculated value not unreasonable in view of the other compounds which were studied.

The reaction path for the formation of  $C_6H_7^+$  is assigned from the evidence of the metastable transition observed at the apparent mass 77. This corresponds to the process  $C_6H_9^+ \rightarrow C_6H_7^+ + H_2$  and eliminates the alternate choice of 3H associated with this ion's production. The value of the calculated heat of formation of  $C_6H_7^+$  is considerably higher than that observed from 1,3-cyclohexadiene (18). The difference might be expected to result from the presumed linear structure of this ion as compared to the probable cyclic structure of the ion formed from 1,3-cyclohexadiene. However, estimates of the proton affinity of hexatriene suggest that the linear  $C_6H_7^+$  ion would also have a heat of formation considerably below our measured value and so we must conclude that the process of its formation involves excess energy.

The  $C_5H_7^+$  formation mechanism is confirmed by the metastable transition observed at 54.7, i.e.  $C_6H_{10}^+ \rightarrow C_5H_7^+ + CH_3$ . The calculated heat of formation is slightly lower than that determined from cyclo- $C_5H_8$  (22) and considerably higher than that which was calculated from cyclo- $C_6H_{10}$  (22). It is unclear from these data as to the possible structure that this ion might exhibit.

The metastable transitions observed at 54.7 and 63 point to the reactions  $C_6H_{10}^+ \rightarrow C_5H_7^+ + CH_3$  and  $C_5H_7^+ \rightarrow C_5H_5^+ + H_2$ , resulting in the following mechanism for the formation of  $C_5H_5^+$ ,  $C_6H_{10}^+ \rightarrow C_5H_5^+ + CH_3 + H_2$ . The literature contains widely divergent values for  $\Delta H_f(C_5H_5^+)$  and those from cyclopentadiene are especially suspect because the shape of the ionization efficiency curve makes the determination of the appearance potential very unreliable. As a result any conclusion concerning the state of this ion is impossible at this time.

For the ions  $C_4H_7^+$ ,  $C_4H_6^+$  and  $C_4H_5^+$  reasonable values for their heats of reaction can be derived on the basis of the mechanisms written. It must be recognized that the processes that are listed are unconfirmed by observable metastable transitions so that other paths leading to higher heats of formation of the ions could be formulated. The results obtained for these cases must be regarded as speculative.

A speculative mechanism for the formation of  $C_4H_4^+$  is listed and gives a reasonable heat of formation reflecting some excess

energy. Other processes might be also written though, so that without further evidence this mechanism has to be conceded as arbitrary.

The appearance potentials of  $C_4H_3^+$ ,  $C_4H_2^+$ ,  $C_3H_5^+$  and  $C_3H_3^+$  are reported. No attempt is made to assign any particular mode for their production from 2,4-hexadiene because of the many equi-energetic paths that can be written for each case. No evidence of metastable transitions which might help in deducing a particular mechanism were observed.

2,5-Dimethyl-2,4-Hexadiene: Table 6 lists the results that were obtained from 2,5-dimethyl-2,4-hexadiene.

The heat of formation of the  $C_8H_{14}^+$  compares well with what was calculated for this ion and is reported. No literature value for this ion has been reported previously, so a comparison of our value is impossible, but the good agreement of the previous compounds with other workers would tend to affirm this particular result. Note the relatively small amount of  $C_8H_{13}^+$  formed in this compound by electron impact (see Table 11) which prohibited the measurement of its appearance potential. A comparison of the 2,4-dimethyl-2,5-hexadiene with the 2,4-hexadiene suggests that the hydrogens on the 2 and 4 carbons are most readily removed once the compound is ionized.

The characteristic reaction of the loss of  $CH_3$  is observed for this compound by the metastable transition at mass 82 corresponding to  $C_8H_{14}^+ \rightarrow C_7H_{11}^+ + CH_3$ . The calculated value of the heat of

formation of the  $C_7H_{11}^+$  based upon this reaction mechanism is reported. Further comment has to be withheld about this ion until it can be examined from other sources.

For the production of  $C_6H_9^+$ , three reactions of different energy are possible. They are loss of  $C_2H_4 + H$ , or  $C_2H_3 + H_2$ , and  $C_2H_2 + H_2 + H$ . Calculation of the corresponding heats of formation give 241, 202 and 160 kcal/mole. Comparing these to our value of 218 kcal/mole for the heat of formation of  $C_6H_9^+$  from 2,4-hexadiene, we tentatively conclude that the loss of  $C_2H_5$  is the most probable one. It is conceivable how excess energy might be realized, but unless gross experimental error was inadvertantly introduced a lower value is quite unreasonable.

Several reactions are conceivable for the formation of  $C_6H_7^+$ . Assuming that the ion is not of a cyclic structure, it would seem reasonable that its heat of formation from this source should be similar to that of  $C_6H_7^+$  from 2,4-hexadiene discussed above. Two of the several processes are given in table 6, along with the resulting value of  $\Delta H_f(C_6H_7^+)$ . A choice is not possible.

The process noted for the formation of  $C_6H_5^+$  is again arbitrary. Other processes can be written with the heat of formation in better agreement with that reported from other compounds, but no good basis exists for one choice over another.

The  $C_5H_7^+$  formation mechanism is established by the metastable transitions observed at 82 and 47.3. These metastable ions are formed

by the reactions  $\text{C}_8\text{H}_{14}^+ \rightarrow \text{C}_7\text{H}_{11}^+ + \text{CH}_3$  and  $\text{C}_7\text{H}_{11}^+ \rightarrow \text{C}_5\text{H}_7^+ + \text{C}_2\text{H}_4$ . The calculated heat of formation is higher than that for the  $\text{C}_5\text{H}_7^+$  ion from either cyclo- $\text{C}_6\text{H}_{10}$  or cyclo- $\text{C}_5\text{H}_8$ . Excess energy appears to be needed for the formation of this ion.

For the remainder of the ions no metastable transitions were observed that could be employed to identify the reaction mechanisms. Consequently for these smaller ions the assignment of a particular mechanism becomes impossible because of many possible choices, each of which yield different values for the ions' heat of formation. Consequently, with these ions, no mechanism and no ionic heats of formation are given.

Mass Spectra. The mass spectra of the various dienes studied are displayed in Tables 7-11. All of these spectra were run at 50 v (nominal) electron energy with the repeller voltage set at 0.7 volt. The ionizing current was 3 microamperes and the source kept at 250°C. Qualitative agreement is exhibited by the mass spectra determined by the use of this instrument with that of previous investigations using different instruments (3). There appears to be discrimination in favor of the fragment ions which had been noted previously (28a ) and appears to be instrumental in character. The cracking pattern (though reproducible) may be altered considerably by changing the various parameters in the source or the analyzer and no satisfactory explanation as to the exact cause can be stated. Discrimination may be due to the detector itself, because different multipliers respond

differently to ions of different composition and energy. However, the greater part of the differences in mass abundances of individual ions between this and other mass spectrometers must be attributed to differences in focusing properties of the instrument. This is particularly critical in the CEC 21-701 because of the additional requirements for control resulting from the presence of the electrostatic field plates in the analyzer. The mass spectra of 2,4-hexadiene and 2,5-dimethyl-2,4-hexadiene are compared with those determined on a CEC-21-110 mass spectrometer. This instrument is employed for compound identification and points out the qualitative agreement of spectra that can be obtained with the CEC-21-701 mass spectrometer. The metastable ion transition data was taken from other sources (3) and from spectra obtained with the CEC-21-110, because the focusing properties of this instrument are such that the known metastable transitions do not appear at the same non integral mass numbers and no correlation between the decomposing ion to its daughter ion could be made.

#### CONCLUSION

The mass spectra and ionization and appearance potentials of the principal ions from some alkadienes have been studied, using the CEC-21-701 mass spectrometer. The ionization and appearance potentials are generally in quite good agreement where comparison can be made. Reaction mechanisms can be postulated in many of the cases through a comparison of the calculated heat of formation with that reported for the ion previously. The use of metastable transition data is a valuable aid in deciding the path for a process and was extensively

used when such information was available. It should be also noted that this kind of analysis tends to become futile when the molecule becomes extensively fragmented because of the increased variety of products that can be formed. Even though excess energy may be involved and detected by a study such as this, the answer as to its distribution among the products or how it could manifest itself, cannot be learned from a study such as this.

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TABLE I  
IONIZATION POTENTIALS

Compound	Ion	This Work I.P. eV	Literature I.P. eV
propadiene	$C_3H_4^+$	$10.15 \pm 0.03$	$10.19^a(49)10.16 \pm 0.02(7)10.0(10)$
1,3 butadiene	$C_4H_6^+$	$9.09 \pm 0.03$	$9.07 \pm 0.01(56)9.08(1a)9.18 \pm 0.02(7)$
1,3 trans-pentadiene	$C_5H_8^+$	$8.70 \pm 0.02$	$8.68(8)$
2,4-hexadiene	$C_6H_{10}^+$	$8.48 \pm 0.04$	$[8.4]^b$
2,5-dimethyl- 2,4-hexadiene	$C_8H_{14}^+$	$7.91 \pm 0.05$	$[7.8]^b$

a) Spectroscopic

b) Calculated using Franklin's group orbital method.

TABLE 2  
APPEARANCE POTENTIALS

PROPADIENE					
Ion	Relative Abundance	A.P.(eV)	Neutral Products	This Work $\Delta H_f$ (kcal/mole)	Literature $\Delta H_f$ (kcal/mole)
$C_3H_4^+$	100.0	$10.15 \pm 0.03$	-	280	$280^a(49)$ , $280^b(7)$ , $282^c(5)$ , $283^c(57)$ , (37), $296^d(8)$
$C_3H_3^+$	89.6	$12.27 \pm 0.04$	H	273	$271^b(7)$ , $270^c(59)$ , $272^d(59)$
$C_3H_2^+$	34.4	$14.34 \pm 0.08$	$H_2$	377	$373^c(10)$ , $369^c(5)$
$C_3H^+$	27.0	$18.56 \pm 0.05$	$H_2 + H$	422	418 (5)
$C_3H_4^{++}$	5.5	$30.24 \pm 0.2$	-	743	-
$C_3H_3^{++}$	5.2	$34.57 \pm 0.1$	H	791	-
$C_3H_2^{++}$	4.5	$32.52 \pm 0.2$	$H_2 ?$	796	-

a) spectroscopic

b) from propadiene

c) from propyne

d) from cyclopropene

TABLE 3  
APPEARANCE POTENTIALS  
1,3-BUTADIENE

Ion	Relative Abundance	A.P. (eV)	Neutral Products	This Work $\Delta H_f$ (kcal/mole)	Literature $\Delta H_f$ (kcal/mole)
$C_4H_6^+$	60.2	$9.09 \pm 0.03$	-	236	235(56), 238(7), 239(35), 260 <sup>a</sup> (7), 264 <sup>e</sup> (5), 275 <sup>b</sup> (37,56)
$C_4H_5^+$	42.5	$12.19 \pm 0.02$	H	255	245 <sup>b</sup> (5), 264 <sup>c</sup> (5)
$C_4H_4^+$	6.6	$13.84 \pm 0.07$	H <sub>2</sub>	345	292 <sup>d</sup> (50), 291 <sup>b</sup> (5) 358 <sup>c</sup> (5)
$C_4H_3^+$	15.9	$16.25 \pm 0.05$	H <sub>2</sub> + H	349	303 <sup>d</sup> (15), 324 <sup>b</sup> (5), 331 <sup>c</sup> (5)
$C_4H_2^+$	17.7	$16.87 \pm 0.05$	2H <sub>2</sub>	415	338 <sup>e</sup> (5), 361 <sup>d</sup> (15)
$C_3H_3^+$	100.0	$11.54 \pm 0.05$	CH <sub>3</sub>	258	264 (6, 5) 272 (59)
$C_2H_4^+$	55.6	$12.59 \pm 0.03$	C <sub>2</sub> H <sub>2</sub>	262	254 (54) (7) (32), 255(55)
$C_2H_3^+$	62.0	$15.68 \pm 0.02$	C <sub>2</sub> H <sub>3</sub>	323	282(28), 283 (20), 286 (7), 285 (30)
$C_2H_2^+$	28.6	$16.46 \pm 0.1$	C <sub>2</sub> H <sub>2</sub> + H <sub>2</sub>	352	317 (11) (56) (37) (57)
$C_4H_3^{++}$	3.4	$35.90 \pm 0.2$	H <sub>2</sub> + H	802	

a) from 1,2-butadiene

b) from 1-butyne

c) from 2-butyne

d) from vinylacetylene

e) from diacetylene

TABLE 4  
APPEARANCE POTENTIALS  
1,3 trans-PENTADIENE

Ion	Relative Abundance	A.P. (eV)	Neutral Products	This Work $\Delta H_f$ (kcal/mole)	Literature $\Delta H_f$ (kcal/mole)
$C_5H_8^+$	52.9	$8.70 \pm 0.02$	-	220	$219^d(8)$ , $222^a(43)$ $227^a(34,35)$ , $252^b(8)$ , $246^c(8)$
$C_5H_7^+$	72.8	$10.93 \pm 0.02$	H	219	217(22), 235(22)
$C_5H_6^+$	5.4	$12.34 \pm 0.06$	H <sub>2</sub>	303	230(44), 239(19) 256(29)
$C_5H_5^+$	10.6	$13.90 \pm 0.05$	H <sub>2</sub> + H	288	271(19), 309(29)
$C_4H_6^+$	2.9	$13.10 \pm 0.1$	CH <sub>2</sub>	227	235(1a,56), 237(43), 228(48)
$C_4H_5^+$	54.9	$12.57 \pm 0.05$	CH <sub>3</sub>	275	245, 264 (13)
$C_4H_4^+$	4.8	$21.12 \pm 0.08$	CH <sub>2</sub> + 2H?	308	292(50), 291(5) 311(38), 314(33)
$C_4H_3^+$	7.6	$16.36 \pm 0.08$	CH <sub>3</sub> + H <sub>2</sub>	362	303(15)
$C_3H_6^+$	26.8	$12.73 \pm 0.03$	C <sub>2</sub> H <sub>2</sub>	259	229(2,40,56) 231(50) 245(55)
$C_3H_5^+$	59.9	$14.20 \pm 0.02$	C <sub>2</sub> H <sub>2</sub> +H	240	232(40), 239(41)
$C_3H_4^+$	52.4	$12.63 \pm 0.02$	C <sub>2</sub> H <sub>4</sub>	297	282(49), 296(8)
$C_3H_3^+$	100.0	$15.16 \pm 0.02$	C <sub>2</sub> H <sub>2</sub> +H <sub>2</sub> +H	263	264(5), 269(7), 270(59)
$C_3H_2^+$	18.6	$20.86 \pm 0.1$	?	?	
$C_5H_8^{++}$	3.1	$24.51 \pm 0.1$	-	584	-
$C_5H_6^{++}$	2.6	$25.41 \pm 0.2$	H <sub>2</sub>	605	-
$C_5H_5^{++}$	1.6	$30.75 \pm 0.2$	H <sub>2</sub> + H	676	-
$C_5H_2^{++}$	5.2	$32.64 \pm 0.1$	?	?	-

a) from 2 methyl-1,3-butadiene

b) from 1,2-pentadiene

c) from 1,4-pentadiene

d) same compound

TABLE 5  
APPEARANCE POTENTIALS

2,4-HEXADIENE

Ion	Relative Abundance	A.P. (eV)	Neutral Products	This Work $\Delta H_f$ (kcal/mole)	Literature $\Delta H_f$ kcal/mole)
$C_6H_{10}^+$	45.2	$8.48 \pm 0.05$	-	213	210(22,35,42,55)
$C_6H_9^+$	11.4	$10.95 \pm 0.03$	H	218	-
$C_6H_7^+$	11.3	$13.42 \pm 0.02$	$H_2 + H$	274	233 (18)
$C_5H_7^+$	100.0	$10.72 \pm 0.05$	$CH_3$	230	$235^a(22), 217^b(22)$
$C_5H_5^+$	10.6	$13.79 \pm 0.04$	$CH_3 + H_2$	301	$271(19)^c, 306(29)$
$C_4H_7^+$	10.1	$13.19 \pm 0.1$	$C_2H_2 + H ?$	215	$205(40), 213(41)$ $225(40)$
$C_4H_6^+$	24.2	$11.53 \pm 0.07$	$C_2H_2 + H_2 ?$	229	$235(56), 238(7)$ $275(56,37)$
$C_4H_5^+$	24.6	$13.23 \pm 0.05$	$C_2H_4 + H ?$	257	$245(5), 264(4)$
$C_4H_4^+$	5.7	$15.41 \pm 0.08$	$2 CH_3 ?$	304	$292(50)$
$C_4H_3^+$	12.2	$18.32 \pm 0.04$	?	?	
$C_4H_2^+$	6.8	$23.64 \pm 0.2$	?	?	
$C_3H_5^+$	84.2	$13.06 \pm 0.02$	?	?	
$C_3H_3^+$	75.3	$14.92 \pm 0.03$	?	?	

a) from cyclo- $C_5H_8$

b) from cyclo- $C_6H_{10}$

c) from cyclo- $C_5H_6$

TABLE 6

## APPEARANCE POTENTIALS

## 2,5-DIMETHYL-2,4-HEXADIENE

Ion	Relative Abundance	A.P. (eV)	Neutral Products	This Work $\Delta H_f$ (kcal/mole)	Literature $\Delta H_f$ (kcal/mole)
$C_8H_{14}^+$	40.7	$7.91 \pm 0.04$	-	179	-
$C_7H_{11}^+$	89.4	$10.80 \pm 0.03$	$CH_3$	212	-
$C_6H_9^+$	13.8	$11.68 \pm 0.1$	$C_2H_5?$	241	218 <sup>a</sup>
$C_6H_7^+$	12.6	$14.42 \pm 0.05$	$C_2H_5+H_2$ $C_2H_4+H_2+H$ ?	305 266	274 <sup>a</sup>
$C_6H_5^+$	23.6	$16.05 \pm 0.1$	$C_2H_5+2H_2$ ?	342	301(38), 303(12), 312 (33)
$C_5H_7^+$	74.4	$12.88 \pm 0.03$	$CH_3+C_2H_4$	247	217 (22), 235(22), 219 <sup>a</sup> , 230 <sup>a</sup>
$C_4H_7^+$	91.6	$13.03 \pm 0.02$	?	?	
$C_4H_5^+$	32.5	$14.60 \pm 0.04$	?	?	
$C_3H_7^+$	40.7	$12.23 \pm 0.06$	?	?	
$C_3H_5^+$	100.0	$14.27 \pm 0.03$	?	?	
$C_3H_3^+$	68.2	$26.52 \pm 0.1$	?	?	

a) this work

TABLE 7  
MASS SPECTRUM @ 50v  
PROPADIENE

m/e Ratio	Ion	Relative Abundance	
		This Work	Literature (3)
40	$C_3H_4^+$	100.0	100.0
39	$C_3H_3^+$	89.6	96.2
38	$C_3H_2^+$	34.4	40.5
37	$C_3H^+$	27.0	32.6
36	$C_3^+$	6.1	9.4
27	$C_2H_3^+$	0.9	0.7
26	$C_2H_2^+$	3.6	4.8
25	$C_2H^+$	2.8	4.6
24	$C_2^+$	1.2	2.7
20	$C_3H_4^{++}$	5.5	3.8
19.5	$C_3H_3^{++}$	5.2	3.9
19.0	$C_3H_2^{++}$	4.5	3.1
15	$CH_3^+$	0.5	0.3
14	$CH_2^+$	4.5	4.0
13	$CH^+$	2.8	3.4
12	$C^+$	3.4	4.1

TABLE 8  
MASS SPECTRUM @ 50v  
1,3-BUTADIENE

m/e Ratio	Ion	Relative Abundance	
		This Work	Literature (3)
54	$C_4H_6^+$	60.2	100.0
53	$C_4H_5^+$	42.5	65.9
52	$C_4H_4^+$	6.6	11.0
51	$C_4H_3^+$	15.9	23.4
50	$C_4H_2^+$	17.7	24.0
49	$C_4H^+$	5.1	6.8
48	$C_4^+$	1.8	1.0
41	$C_3H_5^+$	1.7	0.2
40	$C_3H_4^+$	3.4	3.2
39	$C_3H_3^+$	100.0	90.6
38	$C_3H_2^+$	8.5	5.7
37	$C_3H^+$	5.6	3.5
36	$C_3^+$	2.2	0.6
29	$C_2H_5^+$	3.6	1.0
28	$C_2H_4^+$	55.6	31.7
27	$C_2H_3^+$	62.0	46.3
26.5	$C_4H_5^{++}$	0.3	0.5
26	$C_4H_2^+$	28.6	14.3
25.5	$C_4H_3^{++}$	3.4	2.3
25	$C_4H^+$	4.3	1.8
24	$C_2^+$	1.0	0.2

TABLE 8  
(continued)

MASS SPECTRUM @ 50v

1,3-BUTADIENE

<u>m/e Ratio</u>	<u>Ion</u>	<u>Relative Abundance</u>	
		<u>This Work</u>	<u>Literature (3)</u>
15	$\text{CH}_3^+$	3.6	0.3
14	$\text{CH}_2^+$	4.0	0.5
13	$\text{CH}^+$	2.2	0.2
12	$\text{C}^+$	2.4	0.2

TABLE 9  
MASS SPECTRUM @ 50v  
1,3 trans-PENTADIENE

m/e Ratio	Ion	Relative Abundance	
		This Work	Literature (3)
68	$C_5H_8^+$	52.9	83.5
67	$C_5H_7^+$	72.8	100.0
66	$C_5H_6^+$	5.4	17.6
65	$C_5H_5^+$	10.6	12.4
64	$C_5H_4^+$	1.2	1.1
63	$C_5H_3^+$	4.4	6.8
62	$C_5H_2^+$	3.7	4.7
61	$C_5H^+$	2.1	2.7
54	$C_4H_6^+$	2.9	3.2
53	$C_4H_5^+$	54.9	73.8
52	$C_4H_4^+$	4.8	5.7
51	$C_4H_3^+$	7.6	9.5
50	$C_4H_2^+$	5.3	6.6
49	$C_4H^+$	1.5	1.2
43	$C_3H_7^+$	1.8	0.8
42	$C_3H_6^+$	26.8	25.7
41	$C_3H_5^+$	59.9	50.5
40	$C_3H_4^+$	52.4	45.6
39	$C_3H_3^+$	100.0	88.3

TABLE 9  
(continued)

MASS SPECTRUM @ 50v

1,3 trans-PENTADIENE

m/e Ratio	Ion	Relative Abundance	
		This Work	Literature (3)
38	$C_3H_2^+$	18.6	16.6
37	$C_3H^+$	7.9	7.0
36	$C_3$	1.0	0.4
34	$C_5H_8^{++}$	3.7	2.4
33.5	$C_5H_7^{++}$	0.4	.4
33	$C_5H_6^{++}$	2.6	1.4
32.5	$C_5H_5^{++}$	1.6	1.1
32	$C_5H_4^{++}$	1.0	1.9
31.5	$C_5H_3^{++}$	1.2	1.1
31	$C_5H_2^{++}$	5.2	3.8
29	$C_2H_5^+$	8.7	4.8
28	$C_2H_4^+$	7.7	5.6
27	$C_2H_3^+$	23.7	42.5
26	$C_2H_2^+$	4.8	8.6
15	$CH_3^+$	5.0	6.9
14	$CH_2^+$	1.7	1.5
13	$CH^+$	0.4	0.4
12	$C^+$	0.2	0.3

TABLE 10  
MASS SPECTRUM @ 50v  
2,4-HEXADIENE

m/e Ratio	Ion	Relative Abundance	
		This Work (CEC-21-701)	This Work (CEC-21-110)
82	$C_6H_{10}^+$	45.2	70.6
81	$C_6H_9^+$	11.4	18.1
79	$C_6H_7^+$	11.3	12.4
77	$C_6H_5^+$	4.5	5.9
74	$C_6H_2^+$	1.1	2.1
67	$C_5H_7^+$	100.0	100.0
65	$C_5H_5^+$	10.6	9.9
63	$C_5H_3^+$	2.5	3.5
62	$C_5H_2^+$	1.0	2.1
55	$C_4H_7^+$	10.1	8.6
54	$C_4H_6^+$	24.2	21.2
53	$C_4H_5^+$	24.6	21.3
52	$C_4H_4^+$	5.7	6.2
51	$C_4H_3^+$	17.2	11.4
50	$C_4H_2^+$	6.8	7.0
43	$C_3H_7^+$	2.7	2.3
42	$C_3H_6^+$	12.7	7.1
41	$C_3H_5^+$	84.5	41.2
40	$C_3H_4^+$	14.7	7.8

TABLE 10  
(continued)

MASS SPECTRUM @ 50v

2,4-HEXADIENE

m/e Ratio	Ion	Relative Abundance	
		This Work (CEC-21-701)	This Work (CEC-21-110)
39	$\text{C}_3\text{H}_3^+$	79.0	37.1
38	$\text{C}_3\text{H}_2^+$	8.5	4.6
37	$\text{C}_3\text{H}^+$	2.6	1.8
29	$\text{C}_2\text{H}_5^+$	11.5	5.2
28	$\text{C}_2\text{H}_4^+$	26.3	4.5
27	$\text{C}_2\text{H}_3^+$	46.7	19.4
26	$\text{C}_2\text{H}_2^+$	6.7	3.5
15	$\text{CH}_3^+$	9.2	2.5

TABLE 11  
MASS SPECTRUM @ 50v  
2,5-DIMETHYL-2,4-HEXADIENE

m/e Ratio	Ion	Relative Abundance	
		This Work (CEC-21-701)	This Work (CEC-21-110)
110	$C_8H_{14}^+$	40.7	62.3
109	$C_8H_{13}^+$	1.1	5.7
96	$C_7H_{12}^+$	4.1	
95	$C_7H_{12}^+$	89.4	100.0
94	$C_7H_{10}^+$	3.3	9.5
93	$C_7H_9^+$	10.2	17.1
92	$C_7H_8^+$	2.0	5.8
91	$C_7H_9^+$	6.1	21.4
83	$C_6H_{11}^+$	5.7	15.7
82	$C_6H_{10}^+$	4.1	7.2
81	$C_6H_9^+$	13.8	20.7
80	$C_6H_8^+$	4.9	7.0
79	$C_6H_7^+$	12.6	27.3
78	$C_6H_6^+$	4.1	6.4
77	$C_6H_5^+$	23.6	23.4
70	$C_5H_{10}^+$	6.1	8.7
69	$C_5H_9^+$	12.2	13.8
68	$C_5H_8^+$	16.3	15.4

TABLE 11  
(continued)

MASS SPECTRUM @ 50v

2,5-DIMETHYL-2,4-HEXADIENE

m/e Ratio	Ion	Relative Abundance	
		This Work (CEC-21-701)	This Work (CEC-21-110)
67	$C_5H_7^+$	74.4	56.1
66	$C_5H_6^+$	3.2	5.4
65	$C_5H_5^+$	8.9	11.7
56	$C_4H_8^+$	6.5	11.2
55	$C_4H_7^+$	9.8	60.6
54	$C_4H_6^+$	8.5	8.5
53	$C_4H_5^+$	32.5	31.1
52	$C_4H_4^+$	5.7	7.0
51	$C_4H_3^+$	11.0	14.4
43	$C_3H_7^+$	40.7	36.2
42	$C_3H_6^+$	11.0	18.4
41	$C_3H_5^+$	100.0	99.6
40	$C_3H_4^+$	14.2	15.9
39	$C_3H_3^+$	68.2	66.9
29	$C_2H_5^+$	45.9	21.6
28	$C_2H_4^+$	70.0	12.1
27	$C_2H_3^+$	87.8	12.0
15	$CH_3^+$	27.2	20.0