114
900
THS

PROTON MAGNETIC RESONANCE SPECTRA OF GASEOUS AND LIQUID HYDROCARBONS

Thesis for the Degree of M. S.
MICHIGAN STATE UNIVERSITY
Norman R. Laine
1958

THESIS

LIBRARY
Michigan State
University

PROTON MAGNETIC RESONANCE SPECTRA OF GASEOUS AND LIQUID HYDROCARBONS

By

Norman R. Laine

A THESIS

Submitted to the College of Science and Arts of
Michigan State University of Agriculture and
Applied Science in partial fulfillment of
the requirements for the degree of

MASTER OF SCIENCE

Department of Chemistry

1958

ABSTRACT

The nuclear magnetic resonance spectra of simple gaseous and liquid hydrocarbons were observed under high resolution by use of the model V-4300-2 Varian spectrometer system. A special sample container was constructed of Teflon to contain the gaseous samples under pressures up to 40 atmospheres. Liquid samples were contained in sealed Pyrex tubes.

The chemical shifts (δ) of the peaks in the spectra of liquid propane, propylene, propene-2-d, propyne, allene and the isomeric butenes were measured with respect to benzene and those of gaseous methane, ethane, ethylene, acetylene, propane, propylene and cyclopropane with respect to hydrogen gas mixed with the gas being studied. Where possible nuclear spin-spin coupling constants (J) for the electron-coupled spin-spin interactions between protons in neighboring groups have been obtained also.

The spectra have been interpreted in terms of the chemical shifts and spin-spin coupling constants. In the case of propane the chemical shift and spin-spin coupling constant were found by the method of Anderson and McConnell (7); from the former a value of the electronegativity of the CH_3 group has been derived.

ACKNOWLEDGEMENT

The writer wishes to express his sincere appreciation to Professor M. T. Rogers for his guidance and helpfulness and to Dr. P. T. Narasimhan for his help and suggestions throughout the course of this work and also to the Atomic Energy Commission for a grant supporting this work.

****
****
******
****
**
*

I

II

III

IV

V

VI

VII

VIII

IX

TABLE OF CONTENTS

PAGE

I INTRODUCTION 1

II THEORETICAL 3

III HISTORICAL 10

IV EXPERIMENTAL 16

V RESULTS 23

VI CALCULATIONS 38

VII DISCUSSION 43

VIII SUMMARY 50

IX REFERENCES 52

LIST OF TABLES

TABLE PAGE

I Proton Chemical Shifts of Substituted Hydrocarbons.. 12

II Proton Chemical Shifts of the Halomethanes........ 13

III Proton Chemical Shifts and Electronegativities of Substituents in some Substituted Ethanes....... 14

IV The Electronegativity of the Halogen Groups in the Ethyl Halides................................ 15

V Boiling Points, Vapor Pressures and Purities of Samples Used.................................. 21

VI Chemical Shifts of Gaseous Hydrocarbons........... 35

VII Chemical Shifts of Liquid Hydrocarbons............ 36

VIII Relative Intensities and Separations of the Propane Peaks.................................... 39

FIGURE

1.

2.

3.

4.

5.

6.

7.

8.

9.

10.

11.

12.

13.

14.

15.

16.

17.

18.

19.

20.

LIST OF FIGURES

FIGURE PAGE

1. Orientations and energy levels for $I=\frac{1}{2}$............ 5
2. Simplified apparatus for basic NMR experiment..... 7
3. Diagram of gas sample cell......................... 18
4. Pressure cap for gas sample cell.................. 19
5. Spectrum of H_2 and CH_4 gas mixture................ 26
6. Spectrum of H_2 and C_2H_6 gas mixture............... 26
7. Spectrum of C_2H_4 and CH_4 gas mixture.............. 26
8. Spectrum of H_2 and C_2H_4 gas mixture............... 27
9. Spectrum of H_2 and cyclopropane gas mixture....... 27
10. Spectrum of propane gas.......................... 27
11. Spectrum of propylene gas........................ 28
12. Spectrum of liquid propane....................... 29
13. Spectrum of liquid allene......................... 29
14. Spectrum of liquid propylene...................... 30
15. Spectrum of liquid propene-2-d.................... 31
16. Spectrum of liquid propyne........................ 31
17. Spectrum of liquid butene-1....................... 32
18. Spectrum of liquid trans-2-butene................. 33
19. Spectrum of liquid cis-2-butene................... 34
20. Plot of electronegativity of substituents versus $\Delta CH_3 - \Delta CH_2$ for substituted ethanes............... 37

INTRODUCTION

I INTRODUCTION

Despite the large amount of work done on nuclear magnetic resonance, very little work has been done on the simple gaseous hydrocarbons such as methane, ethane, ethylene, acetylene, propane, etc.. The purpose of this investigation was to obtain chemical shifts and nuclear spin coupling constants for these simple hydrocarbons where conditions for theoretical interpretation should be most favorable.

Because many of the hydrocarbons observed are gases, a cell was constructed to hold gases under a pressure high enough to give a sufficient concentration of nuclei to provide an observable spectrum. Those gases with low vapor pressures were condensed into a glass sample tube and the spectra of the liquids observed.

THEORETICAL

II THEORETICAL (1-4)

A given nucleus will absorb a radiofrequency signal when the signal frequency corresponds to an energy difference between the two nuclear spin energy levels for the nucleus, in an applied magnetic field. The absorption of this signal causes a transition to take place between two of the energy levels. The resulting transition is a nuclear magnetic absorption line. If the nucleus has no spin there will be no absorption of the signal. Because the nucleus has both mass and charge there is an angular momentum and magnetic moment associated with this spin. The magnitude of the nuclear spin angular momentum is $\sqrt{I(I+1)}\ h/2\pi$ and its projection in the direction of an external field is $Mh/2\pi$ (I is the spin of the nucleus and is the maximum allowed value of the magnetic quantum number M). The magnetic moment components in the direction of an external field are

$$\mu_I = \gamma p$$

$$\mu_I = g_I I \mu_n$$

since,

$$\mu_I = p\frac{e}{2mc}$$

$$\mu_I = \frac{Mhe}{2\pi mc}$$

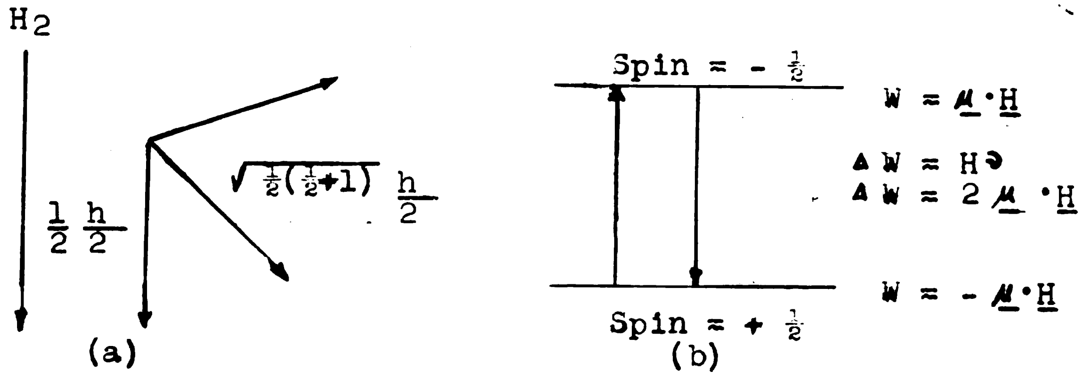
μ_n is the nuclear magneton and is 5.0493×10^{-24} ergs/ gauss.

g_I is an irrational number and is 5.58490 for protons.

γ is the gyromagnetic ratio, i.e., the ratio of the magnetic moment to the angular momentum.

m is the proton mass.

When the nucleus is placed in an external magnetic field, H_o, the field exerts a torque upon the nucleus inducing precession of the spin axis about H_o. The energy of a nucleus in the field is $W = -g_I \mu_I M H_o$. There are $(2I+1)$ quantized orientations and energies of the nucleus in the



H_2
$\frac{1}{2}\frac{h}{2}$
$\sqrt{\frac{1}{2}(\frac{1}{2}+1)}\ \frac{h}{2}$
(a)
Spin = $-\frac{1}{2}$
$W = \underline{\mu}\cdot\underline{H}$
$\Delta W = H\nu$
$\Delta W = 2\underline{\mu}\cdot\underline{H}$
$W = -\underline{\mu}\cdot\underline{H}$
Spin = $+\frac{1}{2}$
(b)

Fig. 1. Orientations (a) and energy levels (b) for $I=\frac{1}{2}$

external magnetic field corresponding to the allowed values I, I-1, ..., -I of the magnetic quantum number, M. For the proton ($I=\frac{1}{2}$), illustrated in Figure 1, there are two energy levels. The frequency separation of the energy levels ($W = \pm \frac{1}{2} g_I \mu_n H_o$) is equal to the precession frequency and is directly proportional to the field strength H_o;

$$h\nu = \Delta W$$

$$h\nu = g_I \mu_n H_o$$

but,

$$g_I = \frac{\mu_I}{I \mu_n}$$

hence,

$$h\nu = \frac{\mu_I H_o}{I}$$

$$\nu = \frac{\mu_I H_o}{I h}$$

$$\nu = \frac{\gamma H_o}{2\pi}$$

and, $2\pi\nu = \omega_0$

so, $\omega_0 = \gamma H_0$ (eq. 1)

Transitions among the nuclei in the different energy levels are induced by a small oscillating field applied to the sample in a radiofrequency coil perpendicular to H_0. A block diagram of the apparatus is pictured in Figure 2. When the radiofrequency is equal to that of the nuclear precession about H_0, resonance absorption occurs. The effect is equivalent to the oscillating field tilting the nuclear magnet with respect to the external field, thus changing the nuclear orientation and energy. This induces an emf in the receiver coil through which the change taking place can be observed.

The resonance frequency of a nucleus is not a constant, but varies according to the compound in which it is present. This is due to the fact that the field at the nucleus is not the same as the applied external field. The paired electrons of the molecule in which the given nucleus occurs give rise to a diamagnetism and alter the effective field at the nucleus. Thus, one must take into account the electronic shielding when calculating the field at the nucleus.

$$H_{nucleus} = H_{applied} - \sigma H_{nucleus}$$

σ is the shielding constant characteristic of the surroundings of the given nucleus.

This shift in the resonance frequency is called the chemical shift. It is now frequently given the symbol, δ,

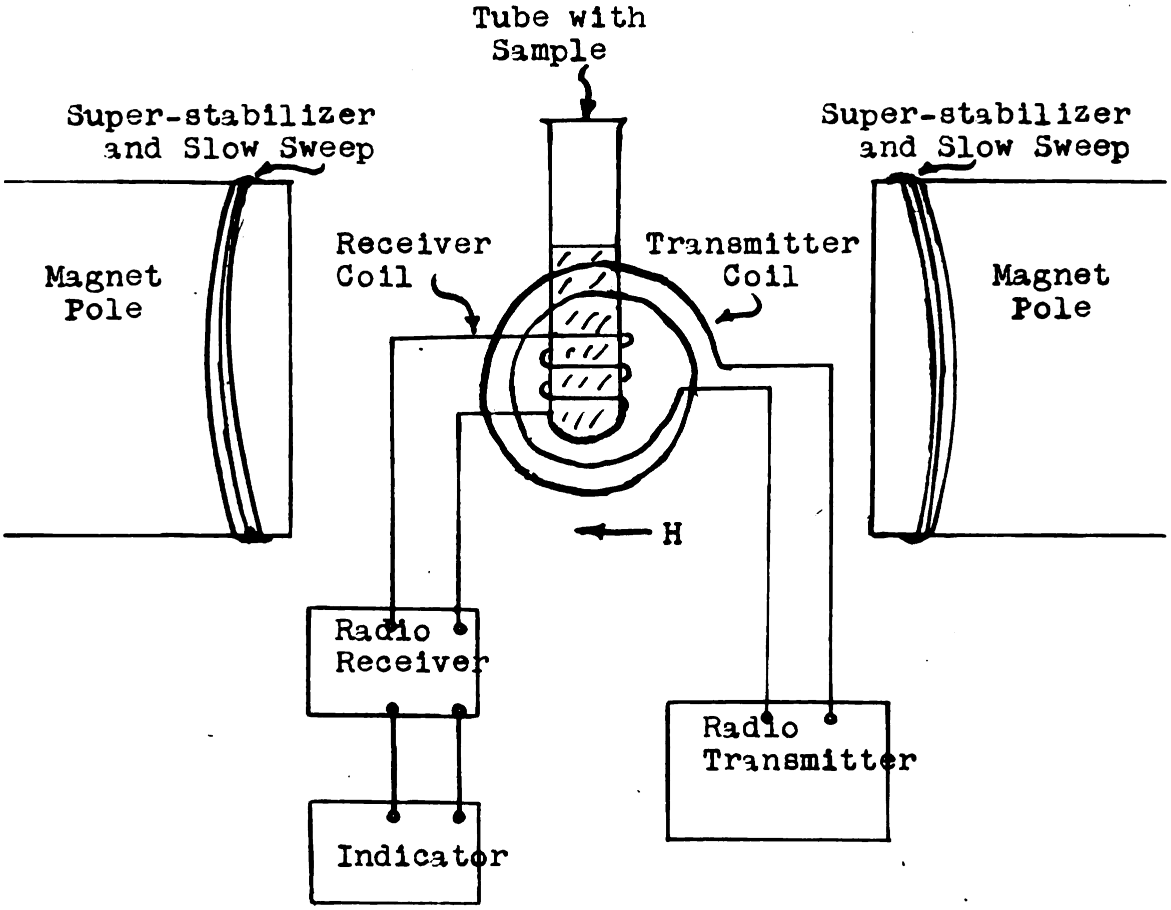

Tube with Sample
Super-stabilizer and Slow Sweep
Super-stabilizer and Slow Sweep
Magnet Pole
Receiver Coil
Transmitter Coil
Magnet Pole
H
Radio Receiver
Radio Transmitter
Indicator

Fig. 2. Simplified apparatus for basic NMR experiment (5)

where

H_c is
field
refere
sured

usuall
chemi
well
shift

diffe
may b
spin
bors
tron
coup
ence
spli
up i
clei
equa
equi
spin
stru

where δ is defined by the equation

$$\delta = \frac{H_c - H_r}{H_r} \times 10^6 \qquad \text{(eq. 2)}$$

H_c is the field at the nucleus being measured and H_r is the field at the reference nucleus. The chemical shift for the reference compound is chosen as zero. Most shifts are measured at a constant frequency.

Each group of non-equivalent nuclei within a molecule usually absorbs at a different frequency. Therefore, the chemical shift can be used for structural determinations as well as determination of chemical shielding. The chemical shift is greater for those nuclei which are more shielded.

In addition to the absorption peaks resulting from the different chemical shifts of non-equivalent nuclei, there may be a fine structure due to the magnetic coupling of the spin of a given nucleus with the nuclear spins of its neighbors through the bonding electrons. This is called the electron-coupled spin-spin interaction. The magnitude of the coupling is governed by the bond type so that valid inferences can be drawn about the character from the observed splittings. The resonance peak of one set of nuclei is split up into a number of peaks by a non-equivalent group of nuclei in the same molecule. The number of component peaks is equal to $2M_I+1$, where M_I equals the total spin of the non-equivalent nuclei in the other group. Electron-coupled spin-spin interactions do not give rise to observable effects for structurally equivalent nuclei. The splitting is usually greatest between directly bonded nuclei, but may be transmitted through several bonds. It is independent of the magnetic field and temperature.

The energy of the spin-spin interaction is proportional to the dot product of the two nuclei,

$$E = J_{ij}\bar{I}_i\bar{I}_j \text{ (6)} \qquad \text{(eq. 3)}$$

where J_{ij} is the constant of proportionality in cycles per second and is called the spin-spin coupling constant. It is simply a measure of the electron-coupled spin-spin interaction.

For a few simple, rigid, symmetrical molecules and for those molecules for which the rapid internal rotation effectively increases the symmetry, J is effectively equal to the multiplet separation in cycles per second. For more complex cases where J and δ are of the same order of magnitude, there are a number of methods for the calculation of the coupling constant, all of which are fairly complex themselves.

The method developed by Anderson and McConnell (7) is the most adaptable. It is an adaptation of the procedure outlined by Van Vleck (8). They showed how to calculate the spin-spin coupling constants and the internal chemical shifts from a knowledge of the intensities and separations of the multiplet peaks.

HISTORICAL

III HISTORICAL

The only work reported with gases under a high pressure has been done by Gutowsky and McClure (9). They built a brass pressure probe to contain samples for the nuclear magnetic resonance spectrometer. The only simple hydrocarbon whose spectrum was obtained is methane. However, in two articles conflicting values for the chemical shift of methane are given. The values given are 3.3 (10) and 9.4 (11), relative to water in both cases. Gutowsky defines the chemical shift as

$$\delta = \frac{H_r - H_c}{H_r} \times 10^5 \qquad \text{(eq. 4)}$$

so his values for the chemical shift must be multiplied by (-10) in order to conform with the definition given in equation 2. The values given above conform to Equation 2.

Meyer, Saika and Gutowsky (12) have measured the chemical shift of a large number of substituted hydrocarbons with reference to water. When they took the average value of these chemical shifts they obtained some values which are in good agreement with the values reported later in this work. These average values along with some selected values of the chemical shifts they measured are given in Table I.

Ogg (13) obtained the nuclear magnetic resonance spectrum for both gaseous and liquid propane. He did not measure the chemical shift. He was interested in finding out if there was a proton absorption shift between the spectrum of the liquid and gas. He found none, but this was probably due to poor resolution. The spectra of both gaseous and liquid propane showed only one peak. The spectrum of the gaseous sample showed a large noise-to-signal ratio indicating a low sample concentration.

TABLE I

PROTON CHEMICAL SHIFTS[*] OF SUBSTITUTED HYDROCARBONS

Compound or group	δ_H
H_2O	0
CH_3-C	+4.1
C_2H_5OH	+4.0
CH_3-C=	+3.3
CH_3-CHO	+3.4
CH_3-C	+3.4
CH_3F	+2.3
CH_3Cl	+2.3
CH_3Br	+2.1
CH_3I	+1.8
CH_2=	-0.5
CH	+2.4
C_6H_5-C CH	+2.5
C=CH-C	-0.8
C_6H_5CH=CH_2	+0.5

---

[*] The reference compound is water and δ is defined by Equation 2.

Meyer and Gutowsky (11) have measured the chemical shift of the halomethanes with respect to methane and their values are shown in Table II.

TABLE II

PROTON CHEMICAL SHIFTS OF THE HALOMETHANES

Compound	δ_H*
CH_4	0
CH_3F	+0.71
CH_2F_2	+0.88
CHF_3	+1.03
CH_3Cl	+0.71
CH_2Cl_2	+0.99
$CHCl_3$	+1.18
CH_3Br	+0.73
CH_2Br_2	+1.01
$CHBr_3$	+1.24
CH_3I	+0.76
CH_2I_2	+0.99
CHI_3 (CCl_4 sol'n)	+0.65

*δ is defined by Equation 4.

Shoolery (14) has measured the chemical shift of some substituted ethanes with respect to ethane. He derived an empirical formula for the correlation of proton magnetic resonance chemical shifts with electronegativities of substituents. This formula is:

$$\text{Electronegativity} = 2.1 + 4.5\,(\delta_{CH_2} - \delta_{CH_3}) \qquad \text{(eq. 5)}$$

The proton chemical shifts of the substituted ethanes are given in Table III.

TABLE III

PROTON CHEMICAL SHIFTS AND ELECTRONEGATIVITIES OF SUBSTITUENTS IN SOME SUBSTITUTED ETHANES

Compound	δ_{CH_3}*	δ_{CH_2}*	Electronegativity	Pauling Electronegativity
C_2H_6	0.00	0.00	2.10	2.1
C_2H_5SH	0.00	0.12	2.64	2.5
C_2H_5I	0.05	0.18	2.68	2.5
C_2H_5Br	0.05	0.21	2.82	2.8
$C_2H_5NH_2$	0.00	0.17	2.86	3.0
C_2H_5Cl	0.02	0.22	3.00	3.0
C_2H_5OH	0.01	0.25	3.18	3.5

*δ is defined by Equation 4.

More recent work along this line has been done by Dailey and Shoolery (15). They studied the chemical shifts in the NMR spectra of a number of methyl and ethyl derivatives in an effort to find out how the electronegativity of an atom changes when it forms a part of different substituent groups. The value of ($\Delta CH_3 - \Delta CH_2$) for the various ethyl halides was plotted against the values of the electronegativity of the corresponding halogen as given by Huggins (16). A straight line resulted which obeyed the following equation:

$$\text{Electronegativity} = 0.02315(\Delta CH_3 - \Delta CH_2) + 1.71 \quad \text{(eq. 6)}$$

The observed values of ($\Delta CH_3 - \Delta CH_2$) along with this equation were used to derive the relative electronegativities of the substituent groups. The linear relationship found for the halogens was assumed to hold for all substituents.

TABLE IV

THE ELECTRONEGATIVITIES OF HALOGENS IN THE ETHYL HALIDES

Group	$\Delta CH_3 - \Delta CH_2$	Electronegativity*
-I	42	2.68
-Br	53	2.94
-Cl	64	3.19
-F	96	3.93

*Electronegativity was found by the use of Equation 6.

Tomita (17) and Thomas, et. al. (18) have studied the NMR spectra of solid methane. Tomita studied the phase diagram of solid methane and Thomas, et. al. studied the variation of the spin-lattice relaxation time with temperature.

EXPERIMENTAL

IV EXPERIMENTAL

The nuclear magnetic resonance spectra of the compounds reported here were all observed with a model V-4300-2 Varian NMR spectrometer at a constant frequency of 40 megacycles per second. A magnet with 12" pole pieces was shimmed for high resolution work and a superhyperstabilizer used to improve the resolution. The chemical shifts of the gaseous compounds were all measured using hydrogen as the reference compound by simultaneous observation of the hydrogen peak and those of the compounds studied. The chemical shifts of the liquid samples were measured with respect to benzene by substituting a benzene sample for the one being studied while maintaining a constant field. The chemical shift of hydrogen with respect to benzene was found. This was done by measuring the separation of the of the hydrogen and benzene peaks from the CH_3 group peak of propene since this peak was observed in the spectra of both gaseous and liquid propene. All of the chemical shifts were then referred to benzene. The chemical shifts of the proton signal from the reference signals were measured by the side band technique of Arnold and Packard (19) by use of a calibrated audio oscillator.

The gaseous samples were contained in a specially made gas cell (Fig. 3) which held the gases up to a pressure of 800 lbs./in.^{2} without bursting. The pressures were measured with an Ascroft diaphragm pressure guage. The pressures of

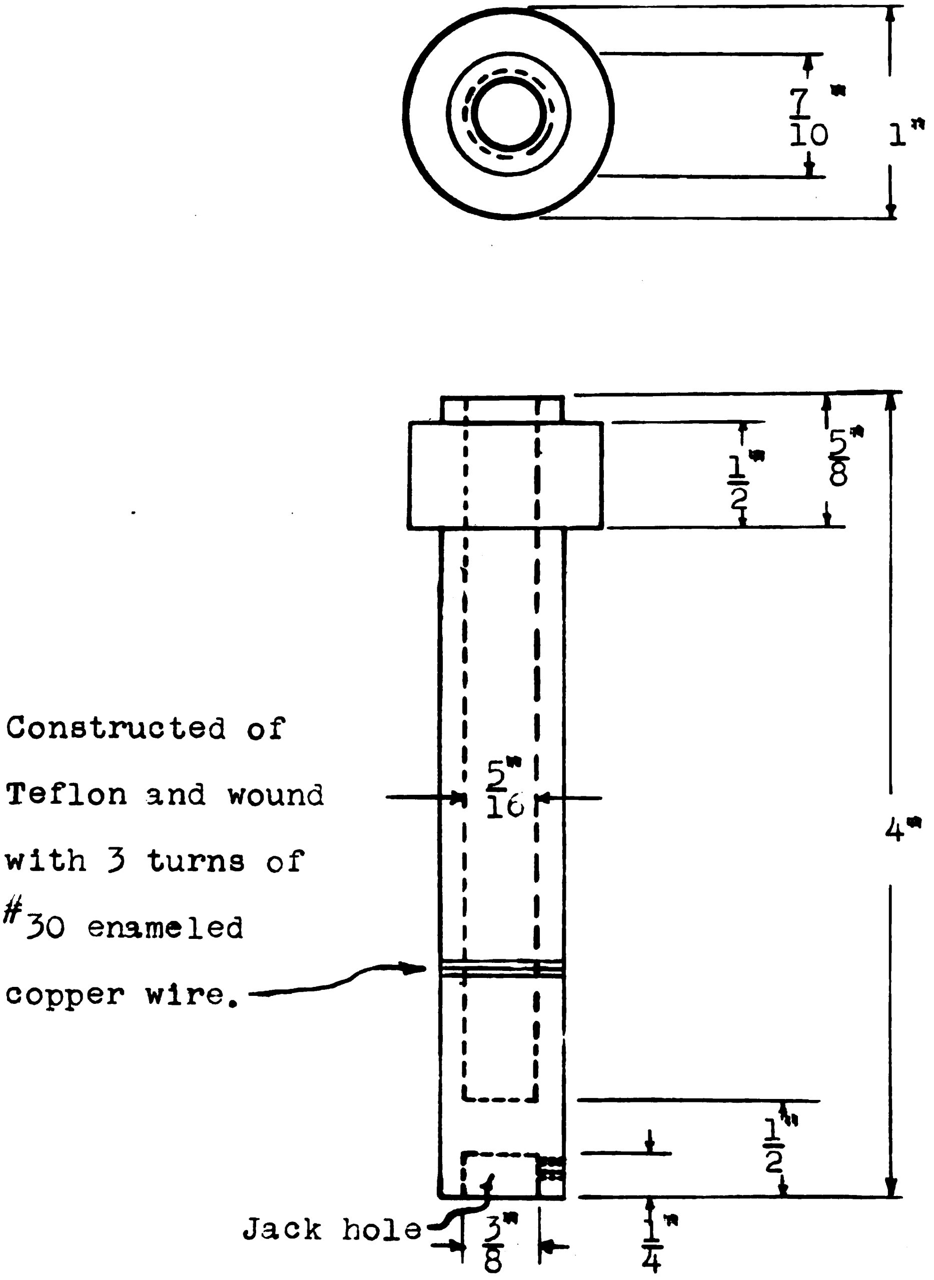

7/10"
1"
1/2"
5/8"
Constructed of Teflon and wound with 3 turns of #30 enameled copper wire.
5/16"
4"
1/2"
Jack hole
3/8"
1/4"

Fig. 3. Diagram of gas sample cell.

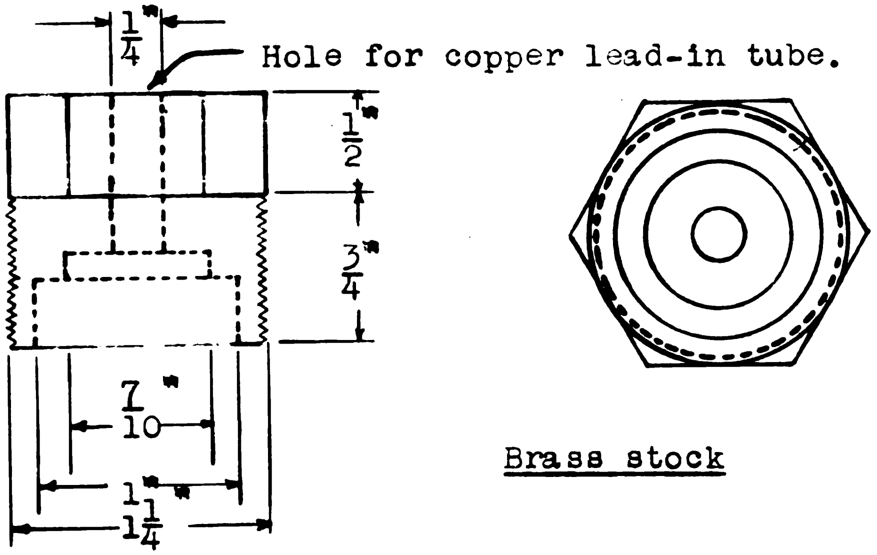

1/4"
Hole for copper lead-in tube.
1/2"
3/4"
7/10"
1"
1 1/4
Brass stock

Fig. 4 a. Male part of pressure cap for gas sample cell.

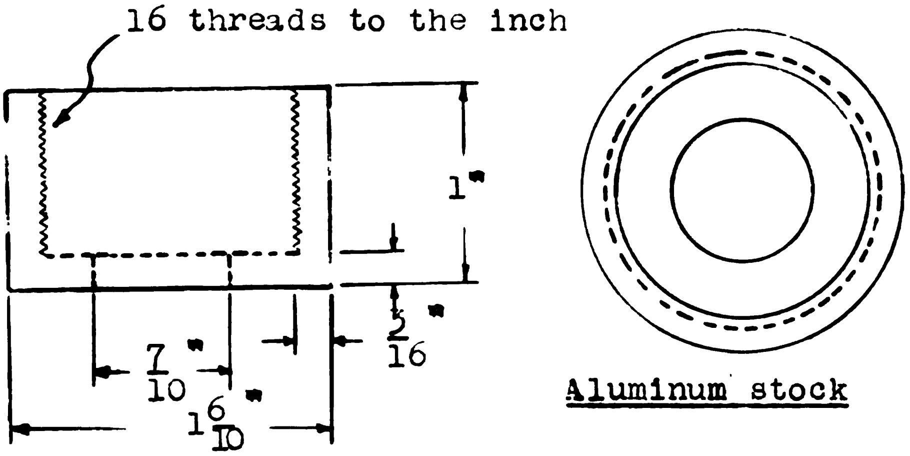

16 threads to the inch
1"
7/10"
2/16"
1 6/10"
Aluminum stock

Fig. 4 b. Female part of pressure cap for gas sample cell.

sample and of the reference gas were approximately equal in each case neglecting deviations from the ideal gas law. In those cases where the spectra of the sample gases were observed without any reference gas present, the pressure of the gas in the cell was equal to its vapor pressure.

All the gaseous compounds which have a sufficiently low vapor pressure were condensed, at liquid air temperatures, into a 5mm O.D. glass tube which was then sealed. The spectra of these liquid samples were then observed.

Purity of Materials

All of the samples were purchased and with one exception were not purified further. A sample of propylene was deoxygenated to determine if oxygen has any effect on the line width of the spectra. The propylene was deoxygenated by repeated condensation at liquid air temperatures followed by warming in vacuo. The deoxygenated sample was then sealed off in a $\frac{1}{2}$" O.D. medium-walled glass tube and its spectrum was observed. The pressure of the gas was about ten atmospheres which is its vapor pressure; the pressure of the gas when it was contained in the Teflon gas cell was about the same. The size of the sample was about the same in both cases. The boiling points, vapor pressures and purities of the samples are given in Table V.

Source of Materials

The following compounds were purchased from the Matheson Co., East Rutherford, N. J.; methane, ethane, ethylene,

TABLE V

BOILING POINTS, VAPOR PRESSURES AND PURITIES OF SAMPLES USED

Compound	Boiling Point (°C)	Vapor Pressure (PSI at 20°C)	% Purity
Hydrogen	-255	2000*	99.8
Methane	-161.4	1500*	99
Ethane	- 88	528	95
Ethylene	-103.9	1250*	99.5
Acetylene	- 88.5	633.5	99.5
Cyclopropane	- 32.9	75	99.5
Propane	- 42.2	109	99
Allene	- 32	100	--
Propylene	- 47.7	139	99
Propene-2-d	- 47.7	139	99
Butene-1	- 6.3	23	99
Trans-2-butene	+ 1.0	15.2	99.3
Cis-2-butene	+ 3.6	12.6	99.7

*Tank pressure

cyclopropane, propane, propylene, propyne and 1-butene.

Acetylene was purchased from the Columbia Organic Chemical Co., Inc., Columbia, S. C..

Propene-2-d was purchased from Merck and Co., Ltd., Montreal, Canada.

Cis-2-butene and *trans*-2-butene were purchased from the Phillips Petroleum Co., Bartlesville, Okla.

Hydrogen was purchased from the Ohio Chemical and Surgical Equipment Co., Cleveland, Ohio.

RESULTS

V RESULTS

The nuclear magnetic resonance spectra of the gases studied are shown in Figures 5 to 11. The reference gas is hydrogen in each case. The NMR spectra of the liquids studied are shown in Figures 12 to 19. The reference in each case is benzene. The chemical shifts are indicated on each figure as well as in Tables VI and VII.

The spectra of the mixtures of gaseous hydrocarbons with hydrogen show only two peaks. With the exception of propylene, one of the two peaks is due to hydrogen and the other is due to the sample. The propylene spectrum (Fig. 11a) shows the internal chemical shift. Actually since there are three non-equivalent proton groups within the propylene molecule, three peaks should appear in the spectrum. Also the spectrum for propane (Fig. 10 a) should show two peaks since there are two non-equivalent proton groups within the propane molecule. The spectra are much more complex for both of these compounds in the liquid phase where not only the internal chemical shift appears, but also the fine structure due to spin-spin coupling.

Much higher resolution is obtained in the spectra of the liquid phase samples than in those of the gas phase. This can also be seen from the line widths. The peaks are much broader in the spectrum of a substance for the gas phase than they are in the spectrum for the liquid phase. It was thought that this line broadening might be due to the presence of a paramagnetic gas such as oxygen in the sample. A sample of propylene was deoxygenated and it was found that this had no effect on the line width. It is possible that some of the broadening results from saturation of the nuclei since rather high RF power must be used with the gaseous samples.

Because the resonance peaks of hydrogen and ethylene were too close together to be resolved, methane was used as the reference gas. Two reference gases were used with propylene. When hydrogen was used, peak A of the propylene spectrum was strengthened (Fig.11 b); when acetylene was used, peak B was strengthened (Fig. 11c). Since the separation of the two reference gases is 137 cycles per second and the separation of the two peaks in the gaseous propylene spectrum is 130 cycles per second, it is obvious that the peaks of the reference gases coincided with the sample peaks and that the chemical shift of peak A with respect to hydrogen is nearly zero.

The electronegativity of the CH_3 group in propane has been plotted in Figure 20 with the electronegativities of the halogen groups in the ethyl halides as given in Table IV.

Each of the spectra, Fig. 5 - Fig. 19(c), represents absorption of radiofrequency radiation (40.0 mc)versus magnetic field strength. Only differences in the latter are used and these are expressed in cycles per second making use of the relation

$$\nu\,(\text{c.p.s.}) = \frac{\gamma}{2\pi}\cdot H$$

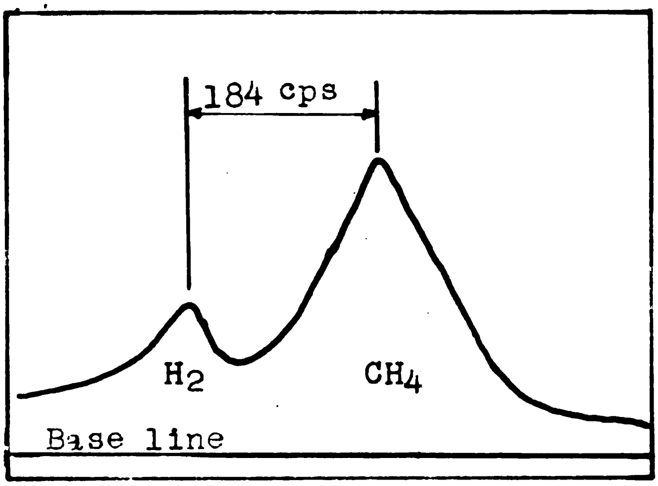


Figure 5. Spectrum of H_2 and CH_4 gas mixture.

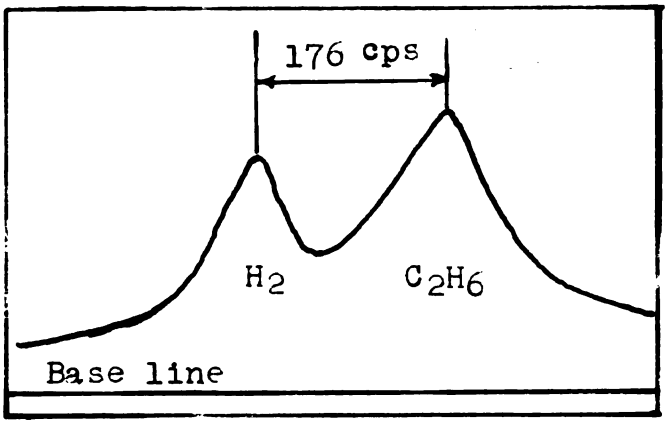


Figure 6. Spectrum of H_2 and C_2H_6 gas mixture.

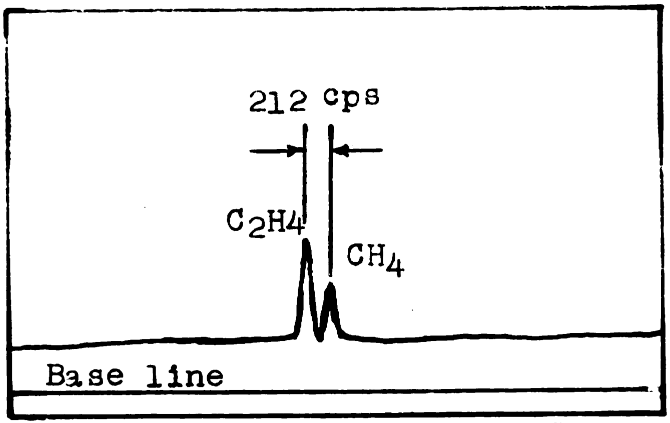


Figure 7. Spectrum of the C_2H_4 and CH_4 gas mixture.

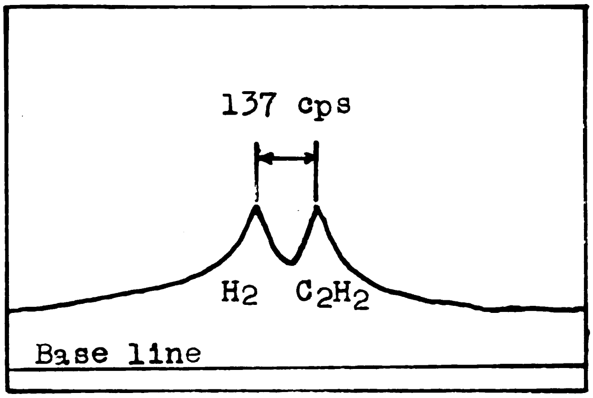


Figure 8. Spectrum of the H_2 and C_2H_2 gas mixture.

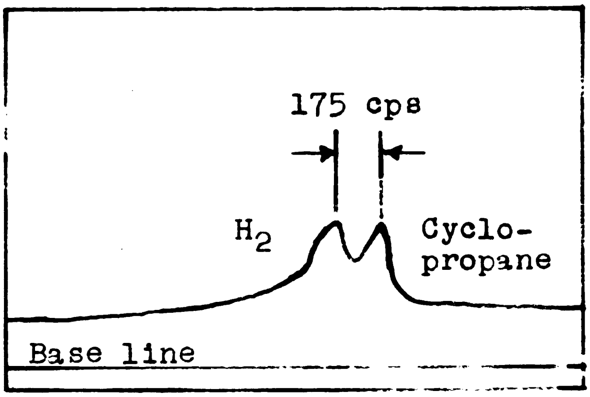


Figure 9. Spectrum of the H_2 and cyclopropane gas mixture.

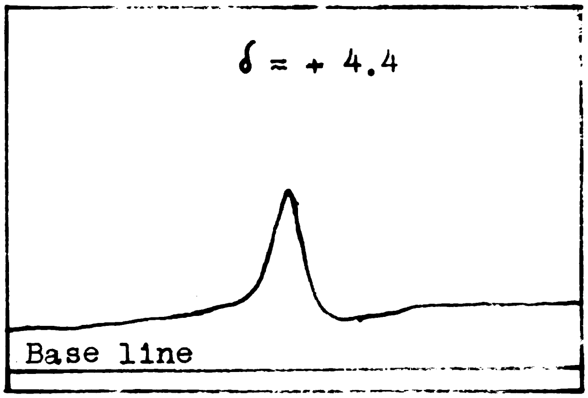


Figure 10 a. Spectrum of propane gas.

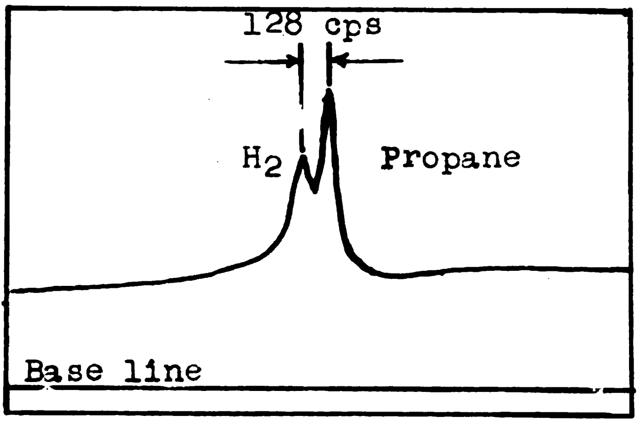


Figure 10 b. Spectrum of H_2 and propane gas mixture.

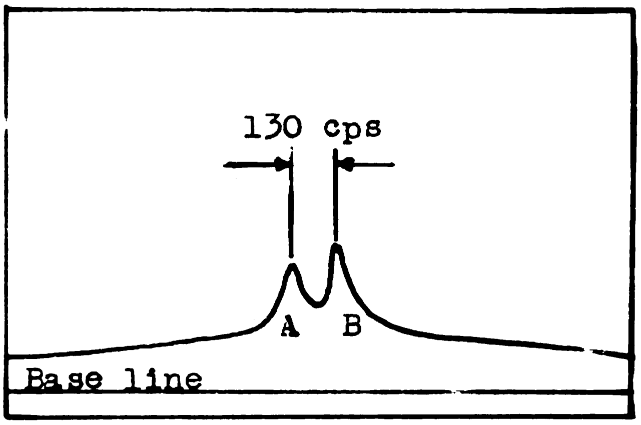


Figure 11 a. Spectrum of propylene gas.

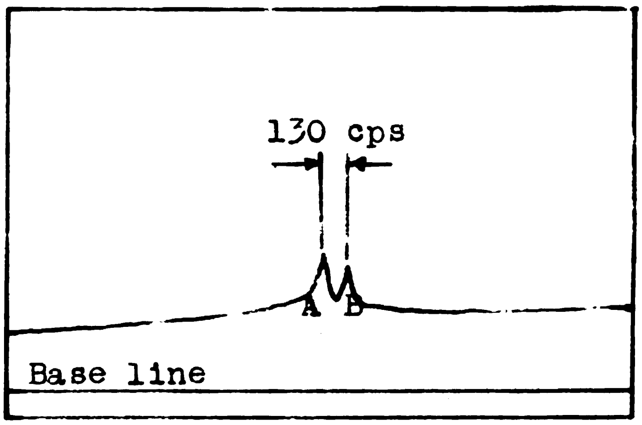


Figure 11 b. Spectrum of H_2 and propylene gas mixture. The H_2 peak falls on peak A of propylene.

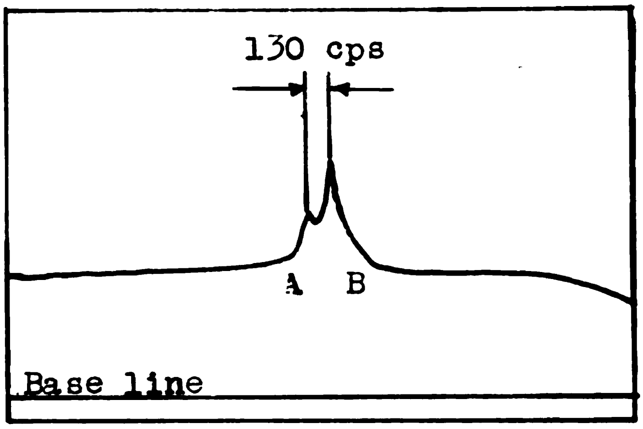


Figure 11 c. Spectrum of acetylene and propylene gas mixture. The acetylene peak falls on peak B of propylene.

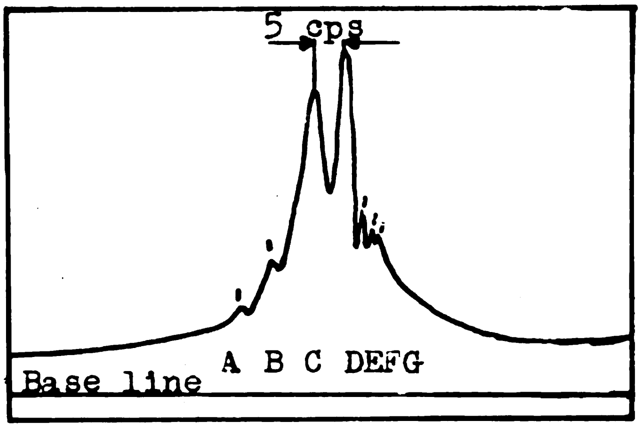


Figure 12. Spectrum of liquid propane.

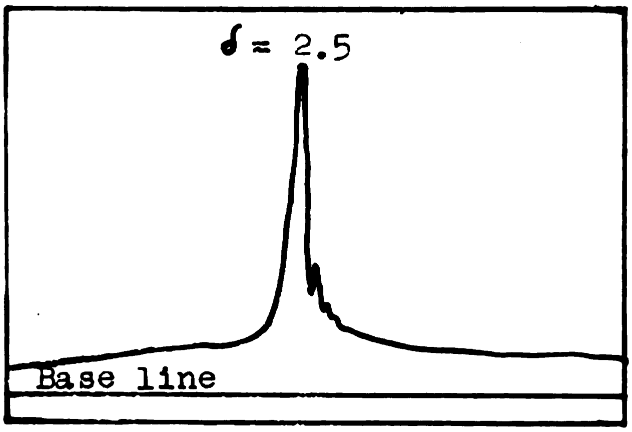


Figure 13. Spectrum of liquid allene.

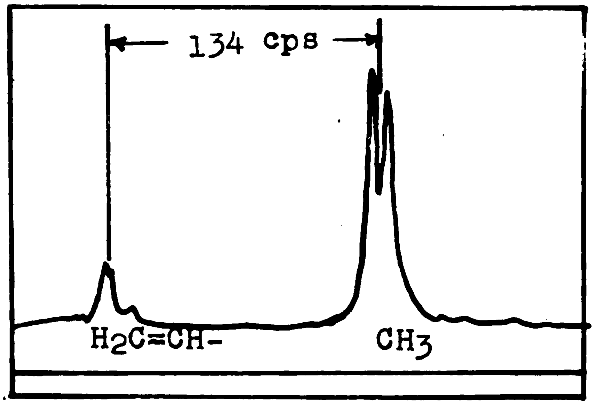


Figure 14 a. Spectrum of liquid propylene.

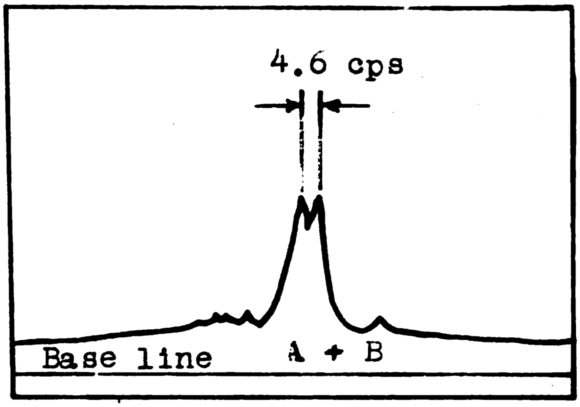


Figure 14 b. Spectrum of the $H_2C=CH-$ group of propylene.

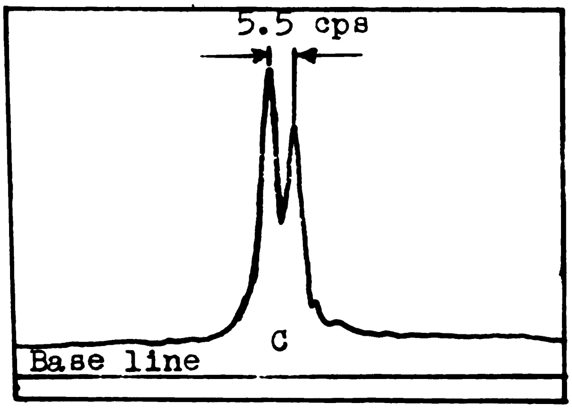


Figure 14 c. Spectrum of the CH_3 group of propylene.

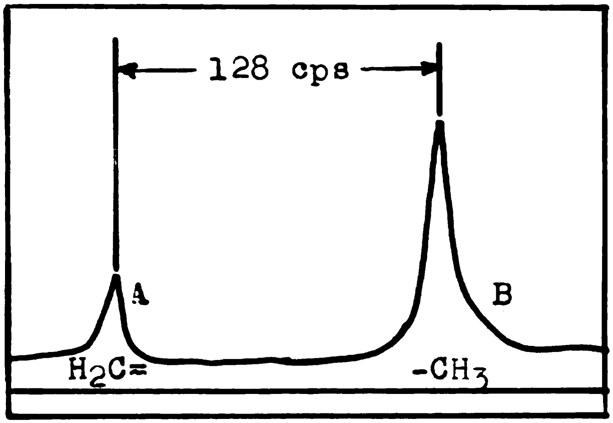


Figure 15. Spectrum of liquid propene-2-d.

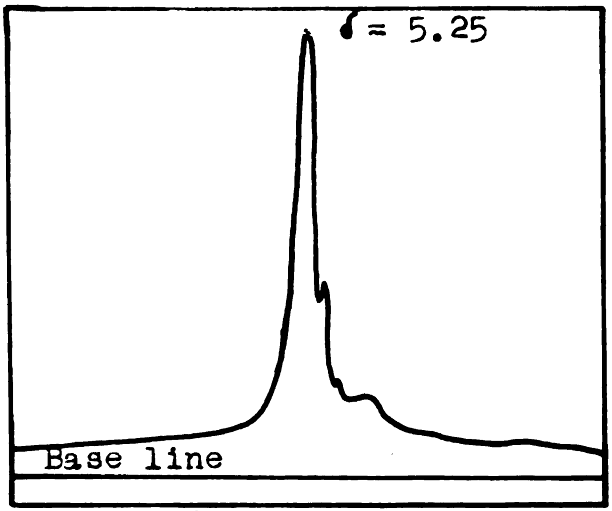


Figure 16. Spectrum of liquid propyne.

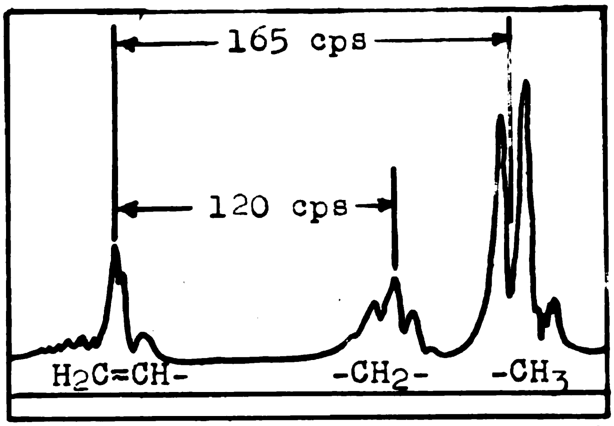


Figure 17 a. Spectrum of liquid butene-1.

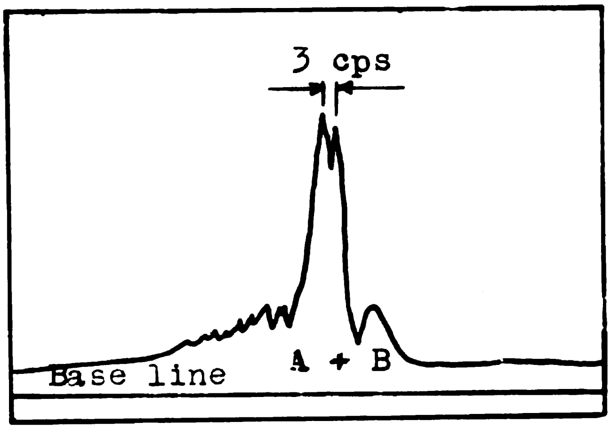


Figure 17b. Spectrum of H_2C=CH- group of butene-1.

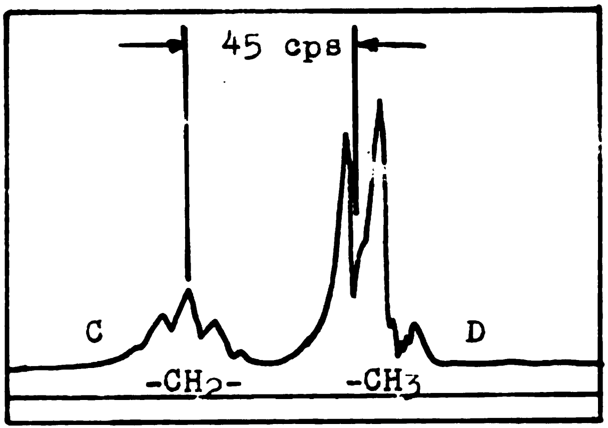


Figure 17 c. Spectrum of CH_2 and CH_3 groups of butene-1.

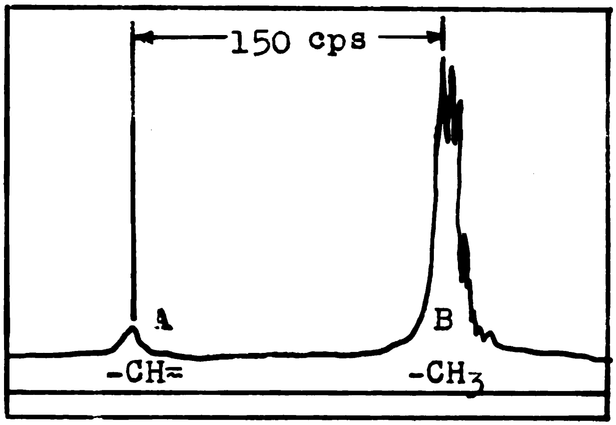


Figure 18 a. Spectrum of liquid *trans*-2-butene.

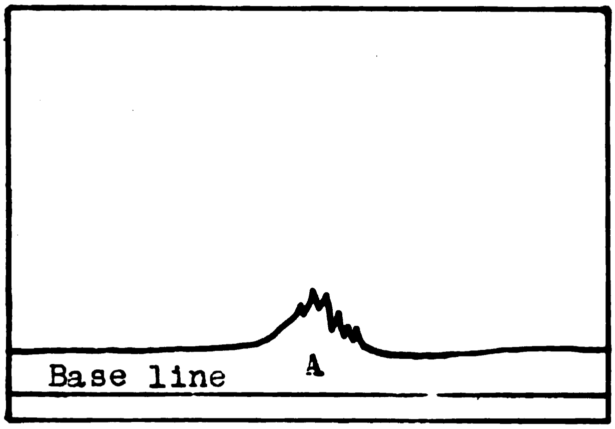


Figure 18 b. Spectrum of -CH= group of *trans*-2-butene.

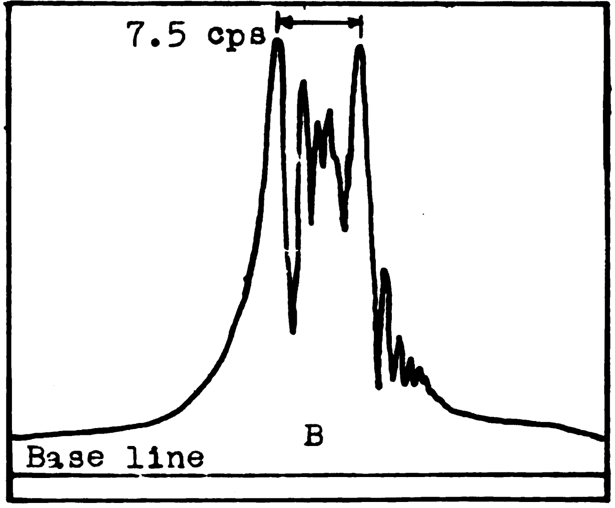


Figure 18 c. Spectrum of -CH$_3$group of *trans*-2-butene.

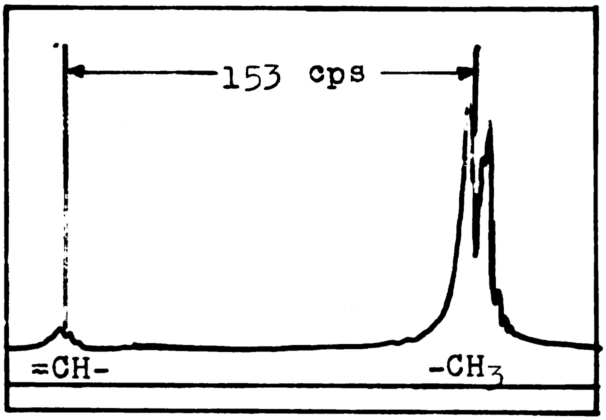


Figure 19 a. Spectrum of liquid *cis*-2-butene.

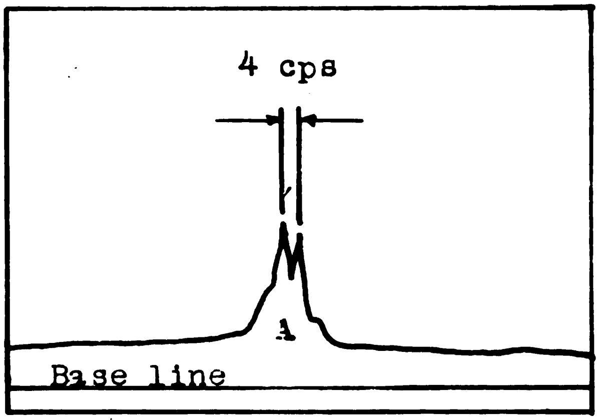


Figure 19 b. Spectrum of the =CH- group in *cis*-2-butene.

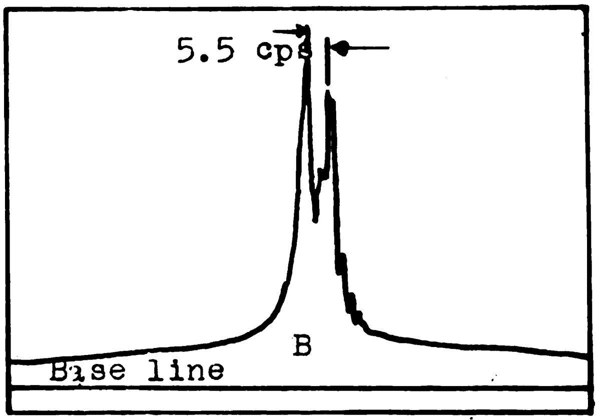


Figure 19 c. Spectrum of the CH$_3$ group in *cis*-2-butene.

TABLE VI

CHEMICAL SHIFTS OF GASEOUS HYDROCARBONS

Gas	Separation from the benzene peak (cps)	Chemical shift[*] δ
Hydrogen	93	2.325
Methane	277	6.925
Ethane	269	6.725
Ethylene	65	1.625
Acetylene	230	5.750
Propane	221	5.525
Cyclopropane	268	6.725
Propylene	Peak A 93	2.325
	Peak B 223	5.575

[*] δ is defined by Equation 2.

TABLE VII

CHEMICAL SHIFTS OF LIQUID HYDROCARBONS

Liquid	Separation from the benzene peak (cps)		δ^*	Δ (cps)	J (cps)
Allene		100	2.500		
Propane	Peak A	240	6.000	14.58	2.75 (a)
	Peak B	245	6.125		
Propylene	Peaks A&B	92	2.325	134.0	5.5 (b)
	Peak C	226	5.650		
Propene-2-d	Peak A	120	3.000	130.0	
	Peak B	248	6.200		
Propyne		210	5.250		
Butene-1	Peaks A&B	80	2.000		
	Peak C	200	5.000		7.5 (a)
	Peak D	245	6.125		
Cis-2-butene	Peak A	67	1.675	153.0	5.5 (b)
	Peak B	220	5.500		0.8 (c)
Trans-2-butene	Peak A	70	1.750	150.0	
	Peak B	220	5.500		

(a) $J_{CH_2-CH_3}$

(b) J_{H-CH_3} (attached to the same carbon atom of the double bond)

(c) J_{H-CH_3} (attached to different carbon atoms of the double bond)

$^*\delta$ is defined by Equation 2.

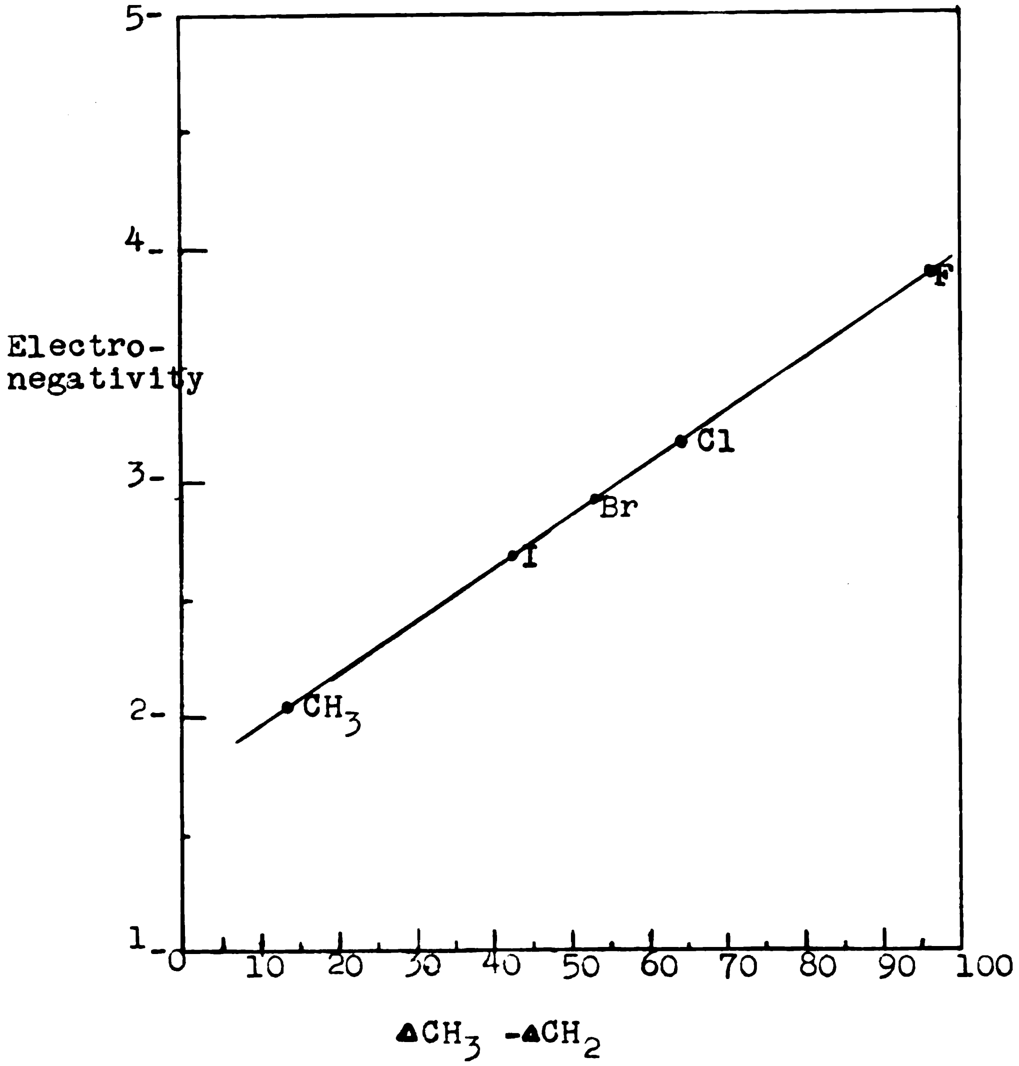


Fig. 20. **Plot of electronegativity of substituent versus $\Delta CH_3 - \Delta CH_2$ for substituted ethanes.**

CALCULATIONS

VI CALCULATIONS

The method used in calculating the spin-spin coupling constant and internal chemical shift of propane is taken from the work of Anderson and McConnell (7).

TABLE VIII

RELATIVE INTENSITIES AND SEPARATIONS OF THE PROPANE PEAKS

Peak	Relative intensities (L)	Distance of peak from center line
A	29	14.5 cps
B	44	9.5 cps
C	140	2.5 cps
D	98	2.5 cps
E	24	5.5 cps
F	14	7.5 cps
G	48	8.5 cps

The spin-spin coupling constant (J_{12}) can be calculated from the folowing equation;

$$(J_{12})^2 = \frac{3}{2I(I+1)(N_1+N_2)}\left\{\frac{\langle(\Delta\omega^a)^4\rangle}{\langle(\Delta\omega^a)^2\rangle} - \frac{(N_1^3+N_2^3)\langle(\omega^a)^2\rangle}{N_1N_2(N_1+N_2)}\right\}$$

The internal chemical shift (Δ) can be calculated from the following equation;

$$(\Delta)^2 = N_1^{-1}N_2^{-1}(N_1+N_2)^2$$

N_1 is the total number of hydrogen nuclei in the CH_3

groups (six), N_2 is the total number of hydrogen nuclei in the CH_2 group (two), and I is the spin of the hydrogen nucleus (one-half).

$\langle(\omega^a)^4\rangle$ and $\langle(\omega^a)^2\rangle$ can be calculated from the following relationship;

$$\langle(\Delta\omega^a)^n\rangle = \langle\{(\omega^a) - \langle\omega^a\rangle\}^n\rangle$$

$\langle\omega^a\rangle$ is the observable mean resonance frequency and is equal to zero because the reference point was chosen halfway between the subgroups.

Therefore,

$$\langle(\Delta\omega^a)^n\rangle = \langle(\omega^a)^n\rangle$$

$$\langle(\Delta\omega^a)^2\rangle = \frac{\sum(\omega^a)^2 L^a}{\sum L^a}$$

$$\langle(\Delta\omega^a)^2\rangle = \frac{(2.5)^2(98)+(5.5)^2(24)+(7.5)^2(14)+(8.5)^2(48)}{98+24+14+48+140+44+29}$$

$$+ \frac{(2.5)^2(140)+(9.5)^2(44)+(14.5)^2(29)}{98+24+14+48+140+44+29}$$

$$\langle(\Delta\omega^a)^2\rangle = \frac{15{,}986}{401}$$

$$\langle(\Delta\omega^a)^2\rangle = 39.86 \ (cps)^2$$

$$\langle(\Delta\omega^a)^4\rangle = \frac{\sum(\Delta\omega^a)^4 L^a}{\sum L^a}$$

$$\langle(\Delta\omega^a)^4\rangle = \frac{(2.5)^4(98)+(5.5)^4(24)+(7.5)^4(14)+(8.5)^4(48)}{98+24+14+48+140+44+29}$$

$$+ \frac{(2.5)^4(140)+(9.5)^4(44)+(14.5)^4(29)}{98+24+14+48+140+44+29}$$

$$\langle(\Delta\omega^{a})^{4}\rangle = \frac{1{,}966{,}448}{401}$$

$$\langle(\Delta\omega^{a})^{4}\rangle = 4903.60 \ (\mathrm{cps})^{4}$$

The value of the spin-spin coupling constant then is;

$$(J_{12})^{2} = \frac{3}{2I(I+1)(N_1+N_2)}\left\{\frac{\langle(\Delta\omega^{a})^{4}\rangle}{\langle(\Delta\omega^{a})^{2}\rangle} - \frac{(N_1^{3}+N_2^{3})\langle(\Delta\omega^{a})^{2}\rangle}{N_1N_2(N_1+N_2)}\right\}$$

$$(J_{12})^{2} = \frac{3}{1(\frac{1}{2}+1)(6+2)}\left\{\frac{4903.60}{39.86} - \frac{(216+8)(39.86}{(12)(8)}\right\}$$

$$(J_{12})^{2} = \frac{1}{4}(123.02 - 92.87)$$

$$(J_{12})^{2} = \frac{1}{4}(30.15)$$

$$(J_{12})^{2} = 7.54$$

$$J_{12} = 2.75 \ \mathrm{cps}$$

The value of the internal chemical shift then is;

$$(\Delta)^{2} = \frac{(N_1+N_2)^{2}}{N_1N_2}\langle(\Delta\omega^{a})^{2}\rangle$$

$$(\Delta)^{2} = \frac{64}{12}(39.86)$$

$$(\Delta)^{2} = 212.45$$

$$\Delta = 14.85 \ (\mathrm{cps})$$

Calculation of the electronegativy of the CH_3 group in propane by use of Equation 6.

$$\begin{aligned}\text{Electronegativity} &= 0.02315(\Delta CH_3 - \Delta CH_2) + 1.71 \\ &= 0.02315(14.58) + 1.71 \\ &= 0.34 + 1.71 \\ &= 2.05\end{aligned}$$

DISCUSSION

VII DISCUSSION

The nuclei which are more shielded are shifted further to the high field side of the spectrum; i.e., have larger positive values of the chemical shift (Eq. 2). The more protons there are grouped around a carbon atom the better shielded these protons will be. On this basis then, methane should have the largest chemical shift of the compounds which were studied. This is so. The chemical shift of methane with respect to benzene is 6.725. The magnetic field in all the spectra shown increases from left to right, so the chemical shift (defined by Eq. 2) also increases from left to right. Therefore, in the spectra shown, the peak on the extreme right is due to the group which is most shielded.

If one went on this basis, one might expect the proton in the CH group to show the least chemical shift. However, this is not so. The chemical shift does not show a consistent decrease in going from ethane to ethylene to acetylene. The shifts for these compounds are 6.725, 1.625, and 5.75 respectively. The acetylene molecule which has two $\equiv CH$ groups has a larger chemical shift than the ethylene molecule which has two $=CH_2$ groups. The reason for this effect is the multiplicity of the bonds attached to the carbon nucleus. The π electrons in the triple bond rotate about the carbon-carbon axis under the influence of an external magnetic field resulting in a Larmor precession which gives rise to an added field at the nucleus (20).

The size of the molecule also affects the chemical shift. The larger the molecule the less the nuclei are shielded and the smaller is the chemical shift. This can be seen in the three compounds methane, ethane and propane. The chemical shift decreases from methane to propane. The respective values of the chemical shift are 6.925, 6.725 and 5.525. However, no quantitative predictions can be made of the value of the chemical shift from either the size or the electronic shielding of the molecule.

Cyclopropane, because of its ring structure is in a class by itself. Its chemical shift is quite high (6.75), signifying that its protons are as well shielded as are the protons in ethane even though cyclopropane consists of CH_2 groups while ethane consists of CH_3 groups. The C-C bonds in cyclopropane are shorter than a usual σ bond indicating some double bond character. This shortening of the C-C bond increases the shielding of the protons and increases the chemical shift.

Propane and propylene were the only two gases capable of showing fine structure which were observed as gases. The vapor pressures of the other substances are too low to give a high enough concentration of nuclei in the gas phase. The other gases - allene, propene-2-d, propyne, 1-butene, *cis*-2-butene and *trans*-2-butene were condensed into a 5 mm O. D. glass sample tube and observed as liquids under a pressure equal to their vapor pressures. Propane and propylene were also observed as liquids and their liquid spectra gave a much higher resolution than their gaseous spectra.

The spectrum of liquid propane (Fig. 12) consists of a single group of multiplets arising from both the CH_3 and CH_2 protons. The fine structure shown is due to the spin-spin coupling between these two groups of non-equivalent protons.

The spectrum of liquid allene shows one peak only. The protons are all equivalent. The chemical shift is 2.5 which indicates that the allene protons are better shielded than the ethylene protons.

The spectrum of liquid propylene (Figs. 14 a to 14 c) shows three groups of multiplets. However, two of the groups of peaks, those due to the CH and CH_2 groups, fall on one-another and are hard to differentiate. This group of peaks is characteristic of the vinyl group (CH_2=CH-). The vinyl group is also present in 1-butene and this same characteristic spectrum appears. The third group of peaks is due to the CH_3 group. This group of peaks is a doublet indicating that there is no spin-spin coupling between the protons in the CH_3 group and the protons in the CH_2 group. The CH_2 group also gives a doublet peak. Thus, both of these groups of protons interact only with the protons in the CH group. The only proton spin-spin coupling effects transmitted across the double bond are those of atoms attached to the carbon atoms of the double bond.

The spectrum of liquid propene-2-d (Fig.15) also bears out this premise. There are just two single peaks present. The peak on the left of the spectrum is due to the CH_2 group and the peak on the right of the spectrum is due to the CH_3 group. There is no spin-spin coupling between the protons of the two groups. The effects are not transmitted across the double bond.

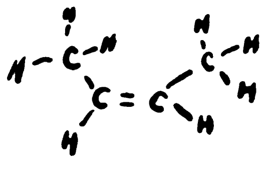
The spectrum for liquid propyne (Fig.16) apparently shows only one peak. The peak due to the $\equiv CH$ group is obscured by the peak due to the CH_3 group. The shielding power of the triple bond is evident here. The CH group has about the same chemical shift as the CH_3 group. The effects of spin-spin coupling are not transmitted across the triple bond either so there is no fine structure.

The spectra of the butenes are quite complicated. There are several non-equivalent groups in the molecules and they interact to produce spectra which are hard to interpret.

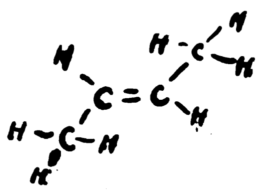
The spectrum of 1-butene (Figs. 17 a to 17 c) consists of four groups of peaks. Two of these peaks are the characteristic peaks of the vinyl group. These are on the left side (low field side) of the spectrum. The CH_3 group, which is the best shielded, is on the right or high field side of the spectrum. The remaining peak is due to the CH_2 group adjacent to the CH_3 group. In Figure 17 b the spectrum of the vinyl group is shown. It is a little different from the spectrum of the vinyl group shown in Figure 14 b. This is because the CH group in 1-butene has more groups to interact with than does the CH group in propylene. The prominent doublet in Figure 17 b is due to the terminal CH_2 group. The protons in the terminal CH_2 group interact only with the proton in the CH group. The remainder of the spectrum in Figure 17 b is due to the proton in the CH group. There is a large amount of fine structure which is partially obscured by the CH_2 peak. Both the CH_3 and CH_2 peaks show some fine structure (Fig. 17 c).

The spectra of the 2-butenes are somewhat alike in that they both show two groups of peaks about the same distance apart. The *trans* compound (Figs. 18 a to 18 c) shows more fine structure in both groups of peaks than does the *cis* compound (Figs. 19 a to 19 c). For both compounds the group of peaks on the low field side of the spectrum is due to the CH groups and the group of peaks on the high field side of the spectrum is due to the CH_3 groups.

The peak for the =CH group of *cis*-2-butene (Fig. 19 b) is a simple quartet indicating that the protons on the ethylenic carbon atoms are only affected by the protons of the CH_3 group on the same side of the double bond. The spin-spin coupling effects are not transmitted across the double bond. However, the spectrum of the =CH group of *trans*-2-butene (Fig 18 b) is composed of several peaks indicating



cis-2-butene



trans-2-butene

that the proton in each =CH group is affected by both CH_3 groups. This seems to indicate tthat the spin-spin coupling effects can be transmitted across the double bond if the two interacting groups are cis to one another.

For cis-2-butene the methyl peak is essentially a doublet indicating that the protons in each CH_3 group interact with the proton in only one =CH group. In Figure 18 a the peak for the CH_3 groups seems to be a quadruplet indicating interactions with both =CH groups. However, Figure 18 c, which shows the CH_3 peaks of trans-2-butene under a higher resolving power, shows a larger number of peaks. These peaks are probably caused by interactions between the CH_3 groups. The CH groups when interacting with the CH_3 groups cause the CH_3 groups to interact with each other. These interactions are weaker than the primary interactions. However, they serve to complicate the spectrum.

The propane molecule has been treated as if it were a substituted ethane. The electronegativity of the CH_3 group has been calculated by the method of Dailey and Shoolery (15). The electronegativities of some substituent groups of ethane have been plotted against the values of (ΔCH_3 -ΔCH_2). This plot is shown in Figure 20. The electronegativity of the CH_3 group has been determined to be 2.05 (see calculations, page 42) using the experimental value of (ΔCH_3 -ΔCH_2) for the CH_3 group found from the propane spectrum.

SUMMARY

SUMMARY

The nuclear magnetic resonance spectra of simple gaseous and liquid hydrocarbons were observed under high resolution by use of the model V-4300-2 Varian NMR spectrometer system. A special container was constucted of Teflon to contain the gaseous samples under pressures up to 40 atmospheres. Liquid samples were contained in sealed pyrex tubes.

The chemical shifts (δ) of the peaks in the spectra of liquid propane, propylene, propene-2-d, propyne, allene, and the isomeric butenes were measured with respect to benzene and those of gaseous ethane, ethylene, acetylene, propane, propylene, cyclopropane, and methane with respect to hydrogen gas mixed with the gas being studied. Where possible nuclear spin-spin coupling constants (J) for the electron-coupled spin-spin interactions between protons in neighboring groups have been obtained also.

The spectra have been interpreted in terms of the chemical shifts and spin-spin coupling constants. In the case of propane the chemical shift and spin-spin coupling constant were found by the method of Anderson and McConnell (7); from the former a value of the electronegativity of the CH_3 group has been derived.

REFERENCES

REFERENCES

(1) J. E. Wertz, Chem. Rev. 55, 829 (1955).

(2) H. S. Gutowsky, Ann. Rev. Phys. Chem. 5, 333 (1954).

(3) J. A. S. Smith, Quart. Rev. (London) 7, 279 (1953).

(4) E. R. Andrew, "Nuclear Magnetic Resonance," Cambridge University Press, Cambridge (1955).

(5) "Radio-Frequency Spectroscopy," Varian Associates Technical Information Bulletin 1, No. 1 (1953).

(6) H. M. McConnell, A. D. McLean and C. A. Reilly, J. Chem. Phys. 23, 1152 (1955).

(7) W. Anderson and H. M. McConnell, J. Chem. Phys. 26, 1496 (1957).

(8) J. H. Van Vleck, Phys. Rev. 74, 1168 (1948).

(9) H. S. Gutowsky and R. E. McClure, Phys. Rev. 81, 277 (1951).

(10) H. S. Gutowsky and C. J. Hoffman, J. Chem. Phys. 19, 1259 (1951).

(11) L. H. Meyer and H. S. Gutowsky, J. Phys. Chem. 57, 481 (1953).

(12) L. H. Meyer, A. Saika and H. S. Gutowsky, J. Am. Chem. Soc. 75, 4567 (1953).

(13) R. A. Ogg, J. Chem. Phys. 22., 560 (1954).

(14) J. N. Shoolery, J. Chem. Phys. 21, 1899 (1953).

(15) B. P. Dailey and J. N. Shoolery, J. Am. Chem. Soc. 77, 3977 (1955).

(16) M. L. Huggins, J. Am. Chem. Soc. 75, 4123 (1953).

(17) K. Tomita, Phys, Rev. 89, 429 (1953).

(18) J. T. Thomas, N. L. Alpert and H. C. Torrey, J. Chem. Phys. 18, 1511 (1950).

(19) J. T. Arnold and M. G. Packard, J. Chem. Phys. 19, 1608 (1951).

(20) J. A. Pople, J. Chem. Phys. 24, 1111 (1956).

CHEMISTRY LIBRARY

~~MAY 2 6 '59~~

~~JAN 2 7 '60~~

~~FEB 2 2 '63~~

Thesis CHEMISTRY LIBRARY
c.2 Laine, Norman R.

M.S. 1958

MICHIGAN STATE UNIVERSITY LIBRARIES
3 1293 03085 5476