U. S. Department of Commerce
National Bureau of Standards

Research Paper RP2045
Volume 43, December 1949

Part of the Journal of Research of the National Bureau of Standards

Mass Spectra of C_5H_8 Isomers

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Mass spectra of ten C_5H_8 isomers are described. These comprise spiropentane, methylenecyclobutane, cyclopentene, six dienes and 1-pentyne. The mass spectrum of each of these compounds has distinctive characteristics, but these are not correlated with the molecular structure in an obvious manner. The ratio of total ionization to that of *n*-butane covers a small range of values from 0.96 to 1.09, and the same range of values is found in other C_5 hydrocarbons. The doubly charged ion spectrum is very prominent in some pentadienes, with $C_5H_2^{++}$ the largest peak.

I. Introduction

The Mass Spectrometry Section has obtained mass spectra of ten C_5H_8 isomers as part of a systematic program of measuring mass spectra of pure hydrocarbons for inclusion in the API Catalog of Mass Spectral Data.[1] Spectra of these isomers have some interesting features in common, although they include compounds that differ greatly in their chemical properties.

Mass spectra have been obtained on a 180° Consolidated mass spectrometer using automatic electron current control and automatic temperature control of the ionization chamber at 245° C. Standard procedures have been followed (see footnote 1) in obtaining mass spectra, and spectra have been measured at both 50- and 70-v ionizing voltage. Data at 70v are quoted here. Intensities are expressed relative to the maximum peak in the spectrum taken as 100, and the sensitivity at the maximum peak (current per unit pressure) is measured in arbitrary units. On the same day the sensitivity of *n*-butane at the mass 43 peak is measured, and the ratio of the two sensitivities affords a measure of sensitivity that is independent of the units used.

We are indebted to the NACA Cleveland Laboratory for making available to us the samples of the rare compounds, spiropentane and methylenecyclobutane. These were considered to be about 99 percent pure, and no recognizable impurities were found in them. 1-Pentyne was made under the direction of Frank Howard in the fuel laboratory of this Bureau and was estimated to be better than 99 percent pure. The NBS standard samples are in general 99.9 percent pure or better.

II. Experimental Results

Table 1 lists the peak heights of some of the more distinctive mass peaks in these spectra. The last two rows give the sensitivity of the maximum peak relative to normal butane and the total ionization relative to *n*-butane. Figures 1 and 2 are plots of the mass spectra, omitting peaks that are less than 2 percent of the maximum peak. Figure 1 includes the cyclics and 1-pentyne, whereas figure 2 gives the dienes except *trans*-1,3-pentadiene, which is almost identical with *cis*-1,3-pentadiene (table 1). In these spectra there are many ions that cannot be obtained by simple dissociation but require a rearrangement of atoms in the dissociation process, and these are marked by asterisks in table 1 and in the figures.

All these compounds give CH_3^+ peaks of the magnitude usually found in hydrocarbons, although four of them (peaks marked by asterisks) do not contain CH_3 radicals. These include the three cyclics that give the smallest CH_3 peaks and also 1,4-pentadiene, which gives a relatively large peak.

The complementary process to production of CH_3^+ is the production of $C_4H_5^+ + CH_3$. For

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[1] Catalog of Mass Spectral Data, American Petroleum Institute, Research Project 44, National Bureau of Standards.

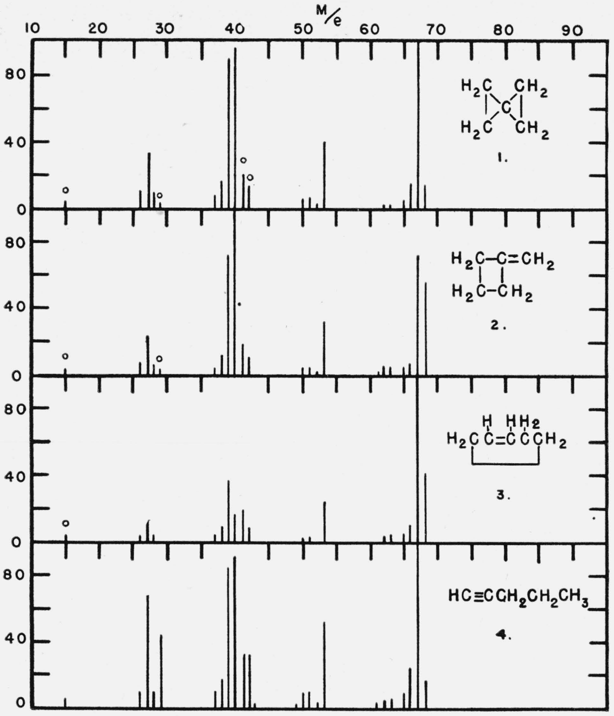

FIGURE 1. *Mass spectra of cyclic* C_5H_8 *isomers and 1-pentyne.*

Ordinates are peak heights relative to a maximum peak height of 100. Dots indicate ions that involve a rearrangement of atoms for their production.

nearly all hydrocarbons, ionization with loss of one carbon atom involves loss of at least three H atoms, and loss of CH_3 is most probable. This is true whether or not CH_3 radicals are contained in the molecule. There is some correlation in these molecules between the height of the CH_3^+ peak and the $C_4H_5^+$ peak; but C_4H_5 is always fairly large, and $C_4H_6^+$ is completely missing even in cases where the terminal radicals are CH_2.

$C_2H_3^+$ is always the largest peak in the C_2 group, and the height does not depend on whether or not this ion can be formed by simple dissociation. The peak is largest in 1,2-pentadiene and in 1-pentyne, which do not yield $C_2H_3^+$ by a single dissociation. By contrast, $C_2H_5^+$ is correlated with the structure and is largest in 1-pentyne and 1,2-pentadiene, which contain ethyl radicals.

The C_3 group of ions shows very distinctive differences. $C_3H_3^+$ is the maximum peak in 1,4-pentadiene and the largest of the C_3 ions in six other compounds. In all but one of these cases it requires multiple dissociation or rearrangement to obtain this ion. $C_3H_4^+$ is the maximum peak in methylenecyclobutane and a large peak in spiropentane and 1-pentyne. $C_3H_5^+$ is larger in the pentadienes than in the other compounds, and its height is roughly correlated with the complementary peak $C_2H_3^+$. Other ions of the C_3 group are not correlated with their complementary C_2 ions. $C_3H_7^+$ is permitted only in 1-pentyne and is observed in this case and is absent or very small in all the other molecules.

The relative heights of $C_5H_7^+$ and $C_5H_8^+$ are also very distinctive for these isomers. In six cases $C_5H_7^+$ is the maximum peak in the spectrum. It is quite unusual in hydrocarbons for ionization with loss of H to be the most probable ionization process, and in our experience propene and toluene are the only other hydrocarbons in which this is true. The molecule ion $C_5H_8^+$ is the maximum peak in two of the pentadienes.

All of these isomers have a metastable transition peak at mass 66 arising from the transition $68^+ \rightarrow 67^+ + 1$. Loss of H in a metastable transition is very rare and is evidently correlated with

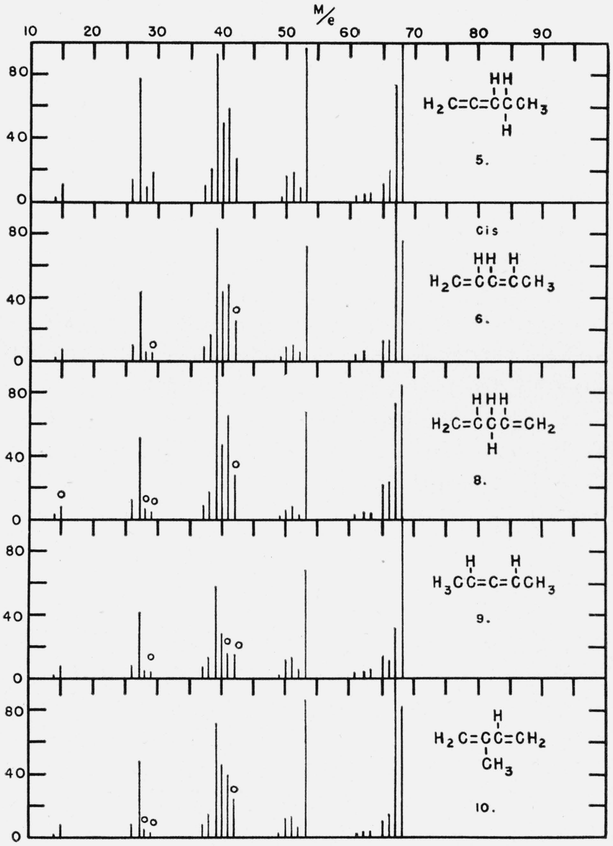

FIGURE 2. *Mass spectra of pentadienes.*

Ordinates are peak heights relative to a maximum peak height of 100. Dots indicate ions that involve a rearrangement of atoms for their production.

TABLE 1. *Relative peak heights in mass spectra of C_5H_8 isomers*

Ion	Reference number									
	1	2	3	4	5	6	7	8	9	10
	Spiro-pentane	Methylene cyclo butane	Cyclo-pentane	1-pentyne	1,2-penta-diene	1-*cis*-3-pentadiene	1-*trans*-3-pentadiene	1,4-penta-diene	2,3-penta-diene	Isoprene
CH_3^+	*3.75	*3.11	*3.21	5.96	10.7	7.29	7.17	*8.16	7.93	6.41
$C_2H_3^+$	33.9	23.0	14.8	68.4	78.7	42.7	41.6	50.9	41.0	47.6
$C_2H_4^+$	8.24	5.64	1.92	7.56	9.2	5.42	5.59	*6.00	5.45	*5.69
$C_2H_5^+$	*2.65	*2.22	*0.90	42.4	18.0	*4.72	*4.85	*4.70	*4.36	*3.77
$C_3H_3^+$	88.8	70.7	36.4	83.9	94.0	82.5	83.7	100	58.6	70.8
$C_3H_4^+$	95.6	100	15.9	89.5	49.3	43.4	45.3	47.3	29.6	44.5
$C_3H_5^+$	*20.3	18.8	19.0	32.0	59.4	48.4	50.6	63.5	*50.2	39.9
$C_3H_6^+$	*12.1	10.4	8.38	31.5	28.0	*24.9	*26.2	*26.6	*15.5	*22.4
$C_3H_7^+$	0	0	0	2.35	*0.30	0	0	0	*0.15	0
$C_4H_5^+$	39.7	31.3	23.4	52.9	97.4	71.9	74.5	68.6	68.5	86.2
$C_5H_7^+$	100	71.6	100	100	75.9	100	100	74.5	31.1	100
$C_5H_8^+$	15.2	56.6	41.6	17.4	100	75.8	79.6	83.6	100	83.2
$C_5H_2^{++}$	2.96	3.29	2.43	5.23	8.21	7.24	7.62	4.91	7.93	4.31
Sensitivity [a]	0.58	0.67	0.99	0.50	0.39	0.526	0.518	0.47	0.62	0.48
Total [a]	.958	.998	1.058	1.060	1.014	1.081	1.087	1.001	1.075	.974

*Ions involving rearrangement of atoms in the dissociation process.
[a] Sensitivity and total ionization relative to *n*-butane.

the relatively high intensity of both the 68 and 67 peaks. Other metastable transitions found in these compounds are of types that recur in many hydrocarbons.[2]

Nine peaks at half integer intervals from mass 30 to 34 come from doubly charged ions C_5^{++}, C_5H^{++}, $C_5H_2^{++}$, etc., to $C_5H_8^{++}$. $C_5H_2^{++}$ is the maximum peak in the doubly charged spectrum, and the relative intensity of this peak is included in table 1. The value 8.21 for 1,2-pentadiene is the highest value ever reported for doubly charged ions in hydrocarbons at 70-v ionizing voltage. The intensity distribution in these doubly charged spectra is similar to that found in all other C_5 hydrocarbons, but the relative intensity is greater than in C_5H_{10} and C_5H_{12} isomers.[3] In other C_5 hydrocarbons, the C_5^{++} peak at 30 is completely masked by the heavy isotope of $C_2H_5^+$; but in most of these compounds the heavy isotope contribution is less than 0.1 percent, and the reality of the C_5^{++} contribution (also about 0.1%) can be established. It is of interest that such an ion exists.

The next to the last row of table 1 gives the sensitivity (ion current per unit pressure) at the maximum peak relative to the sensitivity for the mass 43 peak of *n*-butane. It covers a large range of values from 0.39 to 0.99 and is in general small when there are many large peaks, and large when there are few. Adding the height of all the peaks in the spectrum and multiplying by the sensitivity gives a number proportional to the total ionization. The total ionization relative to the total ionization of *n*-butane is a number that has a small range of values from 0.96 to 1.09, with a mean value of 1.03. For comparison, the three pentanes give values ranging from 0.99 to 1.17, mean 1.09, and the six pentanes have values 0.96 to 1.06, with a mean value of 1.02. It is interesting that C_5H_8 isomers are much like other C_5 hydrocarbons in this respect and all have roughly the same total ionization at constant pressure. Instrumental characteristics may account for some of the small variations observed.

III. Conclusion

This group of isomers is of interest because it comprises a wide variety of chemical classes. Spiropentane is a di-cyclic saturated compound.

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[2] E. G. Bloom, F. L. Mohler, C. E. Wise, and E. J. Wells, J. Research NBS **43**, 65 (1949) RP2005.

[3] F. L. Mohler, E. G. Bloom, E. J. Wells, J. H. Lengel and C. E. Wise; J. Research NBS **42**, 369 (1949) RP1975.

There are two monoolefin cyclics, six diolefins, and one acetylene. It happens that the spectrum of spiropentane is very much like that of the acetylene, 1-pentyne, except for the large $C_2H_5^+$ peak in the latter compound. There are no obvious similarities between compounds of the same chemical class. On the other hand there are several striking characteristics of the spectra as a group; notably the high probability of ionization with loss of one H atom, relatively large peaks at $C_4H_5^+$, at $C_3H_3^+$, or $C_3H_4^+$, and at $C_2H_3^+$. It is evident that the mass spectrum depends markedly on the number of H atoms but not on the chemical unsaturation of the compound. In the ionization and dissociation process there is isomerization, which modifies the original molecular structure. Somewhat similar generalizations can be made concerning the C_4H_6 butadienes and butynes.[4]

Each compound of the group has distinctive characteristics in the mass spectrum to aid in its identification in chemical analysis. The relative height of the $C_5H_8^+$ and $C_5H_7^+$ peaks distinguishes many of the compounds.

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[4] F. L. Mohler, J. Wash. Acad. Sci. **38**, 193 (1948).

WASHINGTON, July 25, 1949.