Mass Spectra of Nonanes

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Mass spectra of the 35 nonanes have been measured with a Consolidated mass spectrometer. Sensitivity (current per unit pressure) at the maximum peak relative to n-butane and total ionization relative to n-butane are given, as well as relative intensities for 18 mass peaks.

Relations between molecular structure and mass spectra are similar to those found in lighter saturated hydrocarbons. Some general relations between mass spectra and molecular structure of saturated hydrocarbons are given, but these are not sufficient to deduce the structure uniquely from the spectrum. The analysis of mixtures of nonanes will, in general, be impossible unless the sample is a cut containing comparatively few components.

I. Introduction

Mass spectra of the 35 nonanes have been measured by the Mass Spectrometry Section of this Bureau as part of the program of measuring mass spectra of pure hydrocarbons. All but one of the spectra have been published in detail in the API Catalog of Mass Spectral Data [1].[1] This paper is a summary of the main features of the nonane spectra, and some empirical relations between the mass spectrum and molecular structure are pointed out. A previous paper has described the mass spectra of the octanes [2]. The nonane isomers give, with few exceptions, quite distinctive mass spectra, so that the mass spectrum affords a valuable method of chemical identification.

II. Experimental Procedure

Mass spectra have been obtained with a 180° Consolidated mass spectrometer equipped with automatic control of the electron current and of the temperature of the ionization chamber. Standard procedures have been followed, except for the method of measuring the vapor pressure in the gas reservoir used to compute the sensitivity (current per unit pressure). This pressure was measured by a diaphragm-type of micromanometer in which

the diaphragm displacement was measured electrically [3]. API tables of serial numbers less than 250 gave sensitivities measured by the conventional method of measuring pressure in a small volume by a mercury manometer and then expanding the vapor into the reservoir. This leads to large errors for compounds like the nonanes, which have low vapor pressures. A correction page has been published in the API Catalog [1].

Thirteen of the nonanes are NBS Standard Samples of purity 99.8 percent or better. We are indebted to several laboratories for samples of the other nonanes. Sixteen were prepared under the direction of Newell C. Cook of Pennsylvania State College, three were prepared by Frank L. Howard of the Engine Fuel Section of the National Bureau of Standards, and three were supplied by F. D. Rossini of the Thermochemistry and Hydrocarbon Section of the Bureau. Most of these samples were considered to be pure compounds of purity estimated to be about 99 percent. In most cases, the mass spectrometer showed no detectable impurities other than nonanes. A few showed insignificant traces of olefins and one compound, 2,2-dimethylheptane, contained a rather large amount of n-octane. Data for this compound are considered inaccurate and provisional.

Mass spectra have been measured with both 50-v and 70-v ionizing voltage, but only measurements at 70-v are given in this paper. Intensities

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[1] Figures in brackets indicate the literature references at the end of this paper.

are given relative to the maximum peak equal to 100, and the limit of sensitivity is about 0.01 on this scale. The sensitivity at the maximum peak is measured in terms of current in arbitrary units per unit pressure in the reservoir. On the same day the sensitivity to n-butane at mass 43 is measured. The ratio of the sensitivity at the maximum peak to the n-butane sensitivity is a molecular property independent of the arbitrary units used.

These spectra have been obtained over a period of about a year, and during most of the time the ionization chamber was thermostated at 245° C. For a few months it was at 275° C. Nine spectra were measured at the higher temperature [1].

III. Results

Table 1 gives the sensitivity relative to n-butane and the total ionization relative to n-butane for the nonanes. Column 1 gives an index number for cross reference to table 2. Column 2 is the name of the compound, column 3 gives the m/e value of the maximum peak, column 4 gives the sensitivity relative to n-butane, column 5 is the sum of all the mass peaks in the spectrum, column 6 is the product of column 4 and column 5 divided by 312 (the sum of the peaks in n-butane). The last column gives the serial number of the mass spectrum in the API Catalog.

About half of the nonanes have the maximum peak at mass 43 and the other half have the maximum at 57. Values for the sensitivity and for the sum of the mass peaks cover about a two-fold range of values with high sensitivity associated with a small value for the sum and vice versa. The product of the two is not constant but has a much smaller range of values. The mean value of total ionization relative to n-butane is 1.94 ±0.13. This is to be compared with values 1.82 ±0.05 for the octanes and 1.68 ±0.04 for the heptanes. The values for octanes and heptanes have been remeasured using a micromanometer, and published values for the octanes [2] are seriously in error.

Table 2 lists the peak heights of 18 mass peaks in the spectra of the 35 nonanes. It includes all the peaks that are large or distinctive in all the spectra. Asterisks mark peaks that cannot be obtained by simple dissociation and involve a rearrangement of atoms in the ionization process.

TABLE 1. *Sensitivity and total ionization relative to n-butane in nonane mass spectra*

Reference	Compound	Maximum Peak	Sensitivity relative to n-butane	Sum of mass peaks	Total ionization relative to n-butane	API serial number
1	n-Nonane	43	1.41	437	1.98	132
2	2-Methyloctane	43	1.31	389	1.64	245
3	3-Methyloctane	57	1.84	302	1.78	246
4	4-Methyloctane	43	1.60	358	1.84	247
5	3-Ethylheptane	57	1.67	378	2.02	335
6	4-Ethylheptane	43	1.60	403	2.07	336
7	2,2-Dimethylheptane	57	------	------	------	------
8	2,3-Dimethylheptane	43	1.95	315	1.87	337
9	2,4-Dimethylheptane	43	1.92	341	2.09	338
10	2,5-Dimethylheptane	57	1.88	346	2.08	339
11	2,6-Dimethylheptane	43	1.61	366	1.89	340
12	3,3-Dimethylheptane	43	1.18	554	2.09	341
13	3,4-Dimethylheptane	43	1.11	522	1.86	342
14	3,5-Dimethylheptane	57	2.04	320	2.09	343
15	4,4-Dimethylheptane	43	1.61	363	1.87	344
16	2-Methyl-3-ethylhexane	43	1.94	357	2.21	345
17	2-Methyl-4-ethylhexane	57	1.68	399	2.14	346
18	3-Methyl-3-ethylhexane	57	1.57	377	1.89	347
19	3-Methyl-4-ethylhexane	57	1.03	567	1.88	348
20	2,2,3-Trimethylhexane	57	2.05	312	2.05	133
21	2,2,4-Trimethylhexane	57	2.50	266	2.13	134
22	2,2,5-Trimethylhexane	57	2.36	271	2.05	135
23	2,3,3-Trimethylhexane	43	1.74	364	2.03	136
24	2,3,4-Trimethylhexane	43	1.79	373	2.15	349
25	2,3,5-Trimethylhexane	43	1.81	324	1.88	137
26	2,4,4-Trimethylhexane	57	1.20	508	1.96	138
27	3,3,4-Trimethylhexane	43	1.13	563	2.04	139
28	3,3-Diethylpentane	57	2.33	261	1.95	140
29	2,2-Dimethyl-3-ethylpentane	57	1.96	310	1.94	248
30	2,3-Dimethyl-3-ethylpentane	57	1.28	452	1.86	350
31	2,4-Dimethyl-3-ethylpentane	43	1.79	310	1.78	249
32	2,2,3,3-Tetramethylpentane	57	1.28	389	1.60	141
33	2,2,3,4-Tetramethylpentane	57	1.29	381	1.58	142
34	2,2,4,4-Tetramethylpentane	57	2.49	219	1.75	143
35	2,3,3,4-Tetramethylpentane	43	1.74	333	1.85	144

Compounds are indicated by a skeleton structural formula in which all hydrogen atoms are omitted. The reference number corresponds to table 1, which gives the names of the compounds. In compound 12 the peak 57^+ is given as 101.5. This is to conform to a formal rule that in the API tables the maximum peak at 50 v is 100, and it happens that in this case 57^+ is less than 100 at 50 v.

Values of the parent ion peak at 128^+ range from 6.4 to 0 with 16 values 0.05 or less. The normal compound has by far the largest parent ion, as is always true in the paraffin series. Sixteen of the 17 compounds with two side chains on a carbon atom account for all the values of 0.05 or less.

TABLE 2. *Mass spectra of nonanes at 70 volts ionizing voltage*

[Values preceded by an asterisk refer to ions that involve a rearrangement of atoms in the ionization process]

Reference	Compound	Relative intensities at m/e values—																	
		27	29	41	43	55	56	57	69	70	71	83	84	85	97	98	99	113	128
1	C C C C C C C C C	29.1	36.7	40.5	100	12.1	16.7	67.0	2.34	11.8	19.7	0.26	6.36	23.3	0.47	2.66	4.53	0.14	6.38
2	C C C C C C C C / C	21.1	23.1	34.2	100	8.89	14.8	51.2	3.34	1.76	26.6	.31	13.5	16.7	.06	0.32	0.82	7.34	2.08
3	C C C C C C C C / C	17.8	27.8	30.7	37.6	8.88	23.9	100	2.63	5.03	8.05	.55	1.84	1.85	.28	12.7	8.84	0.79	1.65
4	C C C C C C C C / C	20.4	21.5	25.7	100	11.8	7.96	25.4	2.62	20.9	27.5	.20	18.2	28.2	.03	3.06	1.42	.82	2.46
5	C C C C C C C / C / C	23.8	28.8	31.2	60.9	13.3	8.00	100	3.50	15.2	14.5	.45	1.50	1.97	.11	20.9	8.84	.04	1.17
6	C C C C C C C / C / C	26.8	24.8	33.0	100	13.0	10.3	*71.4	4.71	3.32	*2.63	.42	20.2	26.8	.09	13.1	4.96	.03	1.27
7	C / C C C C C C C / C	16.5	25	33.2	21.4	7.9	38.8	100	5.0	2.5	13.5	1.48	0.55	0.82	.22	0.03	0.05	2.5	0.74
8	C C C C C C C / C C	20.1	16.8	25.0	100	10.7	9.81	17.1	4.53	3.67	13.4	0.22	28.1	24.1	.02	.12	.33	0.16	1.03
9	C C C C C C C / C C	22.6	18.8	28.9	100	9.04	10.00	25.8	4.02	11.5	21.2	.40	9.51	33.9	.05	.14	.34	.62	0.66
10	C C C C C C C / C C	22.0	29.0	35.1	49.3	8.52	23.1	100	2.44	5.46	10.8	.41	0.77	1.37	.03	3.76	10.5	.61	1.07
11	C C C C C C C / C C	24.0	*19.5	34.3	100	6.57	13.7	46.4	2.96	1.45	24.3	.12	3.67	13.2	.08	0.09	*0.20	8.01	2.80
12	C / C C C C C C C / C	31.5	40.1	44.6	100	20.7	7.28	101.5	3.71	29.4	89.0	.61	0.12	0.44	.12	3.85	15.7	3.65	0.00
13	C C C C C C C / C C	32.8	45.2	48.1	100	22.2	42.2	66.3	3.43	47.3	29.8	.41	2.77	11.60	.10	1.72	6.81	0.18	1.28
14	C C C C C C C / C C	19.0	34.5	31.8	*32.4	9.98	15.9	100	2.74	7.89	13.3	.45	0.11	0.36	.13	3.73	10.4	.32	0.65
15	C / C C C C C C C / C	23.1	19.3	31.1	100	7.20	10.2	*28.1	5.70	0.56	*10.6	.21	14.7	70.1	.05	0.10	0.31	2.39	.00
16	C C C C C C / C C / C	24.1	17.8	30.2	100	13.1	11.6	*35.0	6.98	1.64	*4.10	.44	31.6	27.0	.06	1.05	2.44	0.06	.69
17	C C C C C C / C C / C	26.6	26.1	34.9	75.2	13.8	10.9	100	4.95	13.2	14.6	1.11	2.64	4.15	.21	8.75	12.2	.08	.89
18	C / C C C C C / C / C	21.5	25.4	31.0	61.7	11.6	2.55	*100	6.59	3.48	*6.77	0.72	7.94	28.5	.10	8.05	19.1	1.45	.02
19	C C C C C C / C C / C	32.5	50.5	50.2	*85.1	28.3	34.3	100	4.42	64.2	30.1	.64	0.34	*1.28	.20	4.90	13.0	0.05	1.51

[Values preceded by an asterisk refer to ions that involve a rearrangement of atoms in the ionization process]

Reference	Compound	Relative intensities at m/e values—																	
		27	29	41	43	55	56	57	69	70	71	83	84	85	97	98	99	113	128
20	C CCCCCC C C	13.3	19.2	31.3	23.6	7.37	65.8	100	2.17	5.30	11.2	0.41	0.22	1.67	0.06	0	0.02	1.79	0.03
21	C CCCCCC C C	11.2	21.9	27.1	*13.6	4.81	36.9	100	1.56	4.58	15.2	.59	.12	*0.14	.07	0.04	.11	2.97	.03
22	C CCCCCC C C	11.6	*16.6	26.3	18.9	5.12	37.3	100	1.30	4.32	17.5	.08	.04	.15	.06	0	0	4.31	.05
23	C CCCCCC C C	18.8	13.2	30.5	100	6.83	*14.2	*30.8	10.2	0.92	*9.22	.52	26.4	65.2	.07	0	0	2.10	.00
24	CCCCCC CCC	23.6	24.8	31.6	100	13.1	10.8	29.7	5.14	19.0	31.1	.84	13.2	28.9	.13	.11	.45	0.03	.19
25	CCCCCC CC C	17.0	*12.0	25.1	100	7.18	9.29	23.1	9.19	3.97	14.3	.34	24.0	40.0	.03	.03	*.12	.20	1.49
26	C CCCCCC C C	26.3	25.2	38.8	95.8	15.5	6.59	100	2.51	3.13	83.7	2.60	0.38	0.62	.16	4.38	17.8	3.41	0.00
27	C CCCCCC C C	26.9	36.2	39.6	*100	26.0	5.82	89.3	3.27	72.5	90.1	1.84	.34	*.28	.27	1.54	10.7	2.28	.03
28	C C CCCCC C C	14.3	20.5	24.2	*24.9	8.39	1.64	*100	4.50	1.31	*1.84	0.74	.17	*.12	.05	11.2	19.3	0.04	.00
29	C CCCCC C C C	12.4	20.7	29.2	*23.0	8.91	62.8	100	2.18	8.79	10.9	.72	.29	*.14	.13	0.11	0.59	.98	.00
30	C CCCCC C C C	24.9	22.8	36.2	98.3	13.2	4.01	*100	10.7	3.14	*9.54	2.78	24.8	35.8	.14	4.27	14.5	.99	.00
31	CCCCC CCC C	16.0	10.3	24.2	100	6.87	7.78	*25.9	13.1	1.72	*4.01	0.73	25.0	43.2	.09	0.05	0.35	.04	.16
32	C C CCCCC C C	15.8	21.8	32.4	*63.6	13.2	9.25	100	3.31	28.9	41.8	2.01	1.53	*2.47	.23	.92	9.24	2.07	.00
33	C CCCCC CCC	16.7	*19.2	33.7	62.1	10.5	55.3	100	4.09	13.5	14.3	0.28	1.92	11.8	.45	.05	*.08	0.87	.02
34	C C CCCCC C C	8.21	*16.2	23.2	*7.66	4.01	30.5	100	0.43	0.65	1.90	.15	*.02	*0.03	.11	.11	*.17	2.06	.02
35	C CCCCC CCC	16.3	*8.44	29.0	100	6.35	*1.79	*32.2	14.9	1.58	*2.94	.33	27.1	58.3	.34	.04	.00	0.81	.00

Compound No. 7, 2,2-dimethylheptane, is an apparent exception, but this is probably not significant as it was impure.

The 113^+ peak has values ranging from 8 to 0.03 with about half of the values less than 0.8. There is no obvious correlation with structure except that 10 compounds with ethyl side chains have small 113^+ peaks with an average value of 0.38 percent.

The 99^+ peak has a range of values from 19.1 to 0 with about half the values less than 1. As in the case of the 85^+ peak of the octanes, this peak tends to be large when there is an ethyl side chain or an ethyl terminal radical attached to a carbon atom with a side chain. In 14 compounds without terminal ethyl radicals (excluding *n*-nonane), values range from 1.42 to 0 with an average value of 0.28. In six of these cases production of 99^+ involves a rearrangement of atoms, and the values of 99^+ range from 0.2 to 0. Of the 20 compounds with ethyl radicals, four (21, 24, 29, and 31) have small values of 99^+, and other values are in the range 2.4 to 19.1.

In saturated hydrocarbons, ionization with breaking of a carbon bond and without further dissociation usually gives the largest peaks, and exceptions afford a distinctive feature that is useful in the identification of compounds. Nonanes 3, 4, 5, 6, and 35 have a 98^+ peak, which is larger than the 99^+ peak. In the last case both peaks are very small, but in the first four compounds this peak is a distinctive feature.

The complementary process to loss of an ethyl radical to give 99^+ is the production of the ethyl ion, 29^+. The 29 peak has a range of values from 50.5 to 8.44, and there is a rough correlation between the height of 29^+ and 99^+. Seventeen compounds with 99^+ less than 1 give a 29^+ peak ranging from 8.4 to 25 with a mean value of 18. In 18 compounds in which 99^+ is greater than 1 percent, 29^+ ranges from 17.8 to 50.5 with a mean value of 30.

The 85^+ peak has a range of values from 70 to 0.03 with about half of the values less than 2.5. As in the case of the 71^+ peak of the octanes, the height of the 85 peak depends on whether or not there are isopropyl terminal radicals or *n*-propyl terminal radicals attached to carbon atoms with side chains. Of the 13 compounds without terminal propyl radicals, all except *n*-nonane have peaks less than 2.5. This includes seven com-

pounds in which production of 85^+ involves a rearrangement of atoms. Of the 22 compounds with terminal propyl radicals, four have small 85 peaks, and the others have peaks ranging from 4 to 70 percent.

In five compounds 84^+ is larger than 85^+, but in two of these the peaks are very small. 84^+ is distinctive in 2,3-dimethylheptane and in 2-methyl-3-ethylhexane. It is of interest that in the octanes the compounds 2,3-dimethylhexane and 2-methyl-3-ethylpentane have a 70 peak larger than 71^+. Also, the heptane, 2,3-dimethylpentane has 56^+ larger than 57^+. As all these molecules lose mass 44 in preference to 43, it is evident that the terminal isopropyl radical (the only common structural unit) must be removed with an additional hydrogen atom.

The complementary process to production of 85^+ is the production of 43^+. There is a correlation between the size of the two peaks, but there are many exceptions. 43^+ is the maximum peak in half of the nonanes, and the smallest value is 7.66. It is 100 in 14 of the compounds with terminal propyl radicals and in three other compounds. In one of these, No. 27, production of 43^+ and 85^+ involves a rearrangement of atoms.

71^+ has a range of values from 90 to 1.84 with about half of the values less than 14. In nine cases rearrangement of atoms is required to give 71^+, and these values range from 10.6 to 1.84 with a mean value of 5.7. In 26 cases where 71^+ is permitted, only two, No. 3 and No. 34, have values less than 10.6, and the mean value of 71^+ for the 26 compounds is 26.5. Four molecules with the terminal radical,

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C

CCC

C,

</div>

give the four largest 71^+ peaks.

70^+ is larger than 71^+ in four compounds, 3-ethylheptane, 4-ethylheptane, 3,4-dimethylheptane, and 3-methyl-4-ethylhexane, and in the last two cases it is large and distinctive. The octane, 3,4-dimethylhexane, gives a maximum peak at 56^+ in an ionization process similar to production of 70^+ in 3,4-dimethylheptane.

The ion 57^+ is the maximum peak in 18 of the nonanes, and in three of these, 18, 28, and 30, it requires a rearrangement to give 57^+. There seems to be no correlation in size between 57^+

and the complementary peak 71^+. Thus, for molecules with a tertiary butyl radical, 57^+ is by far the largest peak, and 71^+ is in most cases less than the average height.

Grouping of similar spectra is important in any attempt to analyze mixtures of nonanes. Eight compounds (No. 7, 20, 21, 22, 29, 32, 33, and 34) with terminal tertiary butyl radicals give similar spectra. These spectra closely resemble the octanes with tertiary butyl radicals. There are some differences to distinguish these nonanes. Compounds 20 and 29 have larger 56^+ peaks, and in compound 33, 43^+, 56^+, and 85^+ are larger, while in compound 32, 43^+, 71^+, and 99^+ are larger.

Seven compounds—No. 9, 15, 16, 23, 25, 31, and 35—with terminal propyl radicals at both ends, give similar spectra characterized by a large 85^+ peak with all heavier ions small. Another of these compounds, No. 11, differs by having a large 113^+ peak and a small 85^+ peak.

Compounds 12, 26, and 27 have similar spectra with peaks 43^+, 57^+, and 71^+ all of nearly maximum intensity. These are molecules with a terminal radical

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C

CCC.

C

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One other molecule, 2,2,3,3-tetramethylpentane, consists of this radical and a tertiary butyl radical, and the spectrum combines characteristics of both radicals with 71^+ of intermediate height.

It is to be emphasized that compounds in these groups have spectra that are similar but far from identical, and, with a few possible exceptions, each spectrum has distinctive characteristics that would serve to identify the compound when it is nearly pure.

IV. Conclusions

Mass spectra have been published for all isomers of paraffins with nine or less carbon atoms, and it is of interest to summarize some general rules relating spectra of paraffins to molecular structure.

1. The normal molecule gives the largest parent peak.

2. All compounds with two side chains on a carbon atom give very small parent peaks (0.05 or less).

3. The most probable dissociation processes commonly involve breaking a carbon bond without further dissociation, but there are a number of exceptions. Often these exceptions occur in molecules with a common structural unit.

Thus, molecules containing a terminal radical,

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CCC,

CC

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lose mass 44 in preference to mass 43.

4. Nonanes and octanes with a terminal tertiary butyl radical have similar spectra with 57^+ by far the largest peak.

5. In molecules with terminal ethyl or propyl radicals, loss of these radicals is relatively probable.

6. Peaks involving rearrangements are, in general, small with many exceptions for 43^+ and 57^+ but not for other peaks.

7. Either 43^+ or 57^+ is the maximum peak for paraffins with more than three carbon atoms. The only clear exception is the octane 3,4-dimethylhexane, which has a maximum peak at 56^+, but in 2,3-dimethylpentane, 56^+ and 43^+ are essentially equal.

8. The total ionization relative to n-butane is roughly constant for isomers and increases with increasing molecular weight.

Rules 4 and 5 often conflict, for if there is a terminal butyl radical the rest of the structure does not influence the spectrum appreciably. This accounts for some of the instances noted above where nonanes with terminal ethyl and propyl radicals have small 99^+ and 85^+ peaks. There are other unrecognized factors that influence the spectrum, and the rules are not sufficient to deduce the structure from the observed spectrum.

It will be a long time before mass spectra of all the decanes have been measured, but spectra of paraffins with 10 or more carbon atoms can be measured, and such spectra can give incomplete information about the structure of pure compounds of doubtful structure.

The analysis of mixtures of nonanes will, in general, be difficult or impossible unless the sample is a narrow cut containing comparatively few compounds. The practical experience in analyzing mixtures of octanes [4] will be directly applicable to nonane analysis. In a complicated mixture it would be necessary to analyze for groups with similar spectra as a group using an average pat-

tern. Comparable difficulties will be encountered in any method of analysis because of the great number of isomers.

V. References

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