Metastable Transitions in Mass Spectra of Fifty-Six Hydrocarbons

By Evelyn G. Bloom, Fred L. Mohler, Jonathan H. Lengel, and C. Edward Wise

In the mass spectra of 56 saturated and unsaturated hydrocarbons, all the observable metastable transitions have been identified. In 362 cases, there are 32 different transitions involving loss of masses 2, 15, 16, 26, 27, 28, 29, 30, 42, and 44. The occurrence of a metastable transition depends on the intensity of both the initial ion peak and the final ion peak.

I. Introduction

The mass spectrum of a hydrocarbon as obtained in a gas analysis mass spectrometer shows peaks at integral mass numbers equal to the molecular weight of the compound and its dissociation products. In addition to these peaks there are commonly found some small and abnormally wide peaks with maxima that are in general at nonintegral mass numbers. Hipple, Fox, and Condon[1][2] have made a detailed experimental study of these abnormal peaks and have given a theoretical explanation. They arise from ions that dissociate after they have traversed the ion-accelerating field. If an ion of mass m_i dissociates immediately after traversing the electric field into an ion of mass m_f and a neutral particle, then the apparent mass m_a of the ion is given by the relation

$$m_a = m_f^2 / m_i. \qquad (1)$$

Because the initial ion does not dissociate at a definite point but over a range of positions, the resulting ion peak is broad and diffuse. Hipple, et al.[1] verified this theory by showing that the kinetic energy of the final ion was reduced in proportion to the mass lost by measuring the stopping potential applied to the ion collector that would reduce the diffuse peak to zero. Thus, if the ion-accelerating potential is V and the ion breaks in half, then a stopping potential of $V/2$ is sufficient to stop the ionized fragment that has only half of the kinetic energy. They ascribed this dissociation phenomenon to excited states of the initial ion, which spontaneously go to the dissociated state with a rather long "life" according to the relation

$$n_t = n_0 e^{-t/\tau}, \qquad (2)$$

where n_0 and n_t are the number in the initial state at zero time and time t. Hipple[3] has measured values of the life τ by measuring relative peak heights with different electric fields drawing ions from the ionization chamber and finds values of the order of 10^{-6} second. The dissociating ions are termed metastable ions, because the life of the initial state is long compared to most radiative transitions.

The authors have been making systematic measurements of mass spectra of pure hydrocarbons and tabulating results in the form of tables published by the American Petroleum Institute, Research Project 44.[4] The tables present intensities of mass peaks relative to a value 100 for the maximum peak in the spectrum and include all peaks of intensity 0.01 or greater. Spectra at ionizing voltages of 50 and 70 volts are given. All measurable peaks involving metastable transitions have been recorded, and it has been possible to identify the transitions involved in nearly every case. Mass spectra of 56 compounds have been published to date.

The following compounds have been included in this study: All saturated isomers (40 in all) from

[1] J. A. Hipple, R. E. Fox, and E. U. Condon, Phys Rev. **69**, 347 (1946).

[2] J. A. Hipple and E. U. Condon, Phys. Rev. **68**, 54 (1945).

[3] J. A. Hipple, Phys. Rev. **71**, 594 (1947).

[4] Catalog of mass spectral data, tables 1 to 56, American Petroleum Institute, Research Project 44, National Bureau of Standards.

methane through the C eights; unsaturated compounds—ethylene, propylene, four butenes, six pentenes, two butadienes, and two butynes. All these compounds except methane show from 1 to 11 metastable transitions. In all, 362 have been recorded and the transitions identified. This paper is a survey of the detailed data that have been published in the API catalog (see footnote 4). Enough cases have been covered to permit some general conclusions to be drawn concerning the occurrence of metastable transitions.

II. Experimental Conditions

A consolidated mass spectrometer has been used in this research, and spectra have been obtained with uniform procedures described in detail in a descriptive sheet published with the API catalog of mass spectra (see footnote 4).

In this spectrometer, ions produced by an electron beam at 50 or 70 volts are drawn out of the ionization chamber by a small field, accelerated by an ion-accelerating voltage and bent through 180° in a homogeneous magnetic field. In obtaining the spectra, the magnetic field is held constant and the ion-accelerating voltage varied. The small draw-out potential is about 1 percent of the ion-accelerating voltage. That is, it is a variable potential varying inversely as the apparent mass of the ion.

The ion current is recorded by four galvanometers with sensitivities in the ratios 1 to 1/3 to 1/10 to 1/30. A compound is run at a pressure to give nearly full-scale deflection for the maximum peak on the 1/30 scale and a peak of 0.01 percent of maximum is detectable under optimum conditions. Figure 1 illustrates a part of the record of the n-butane spectrum showing the four galvanom-
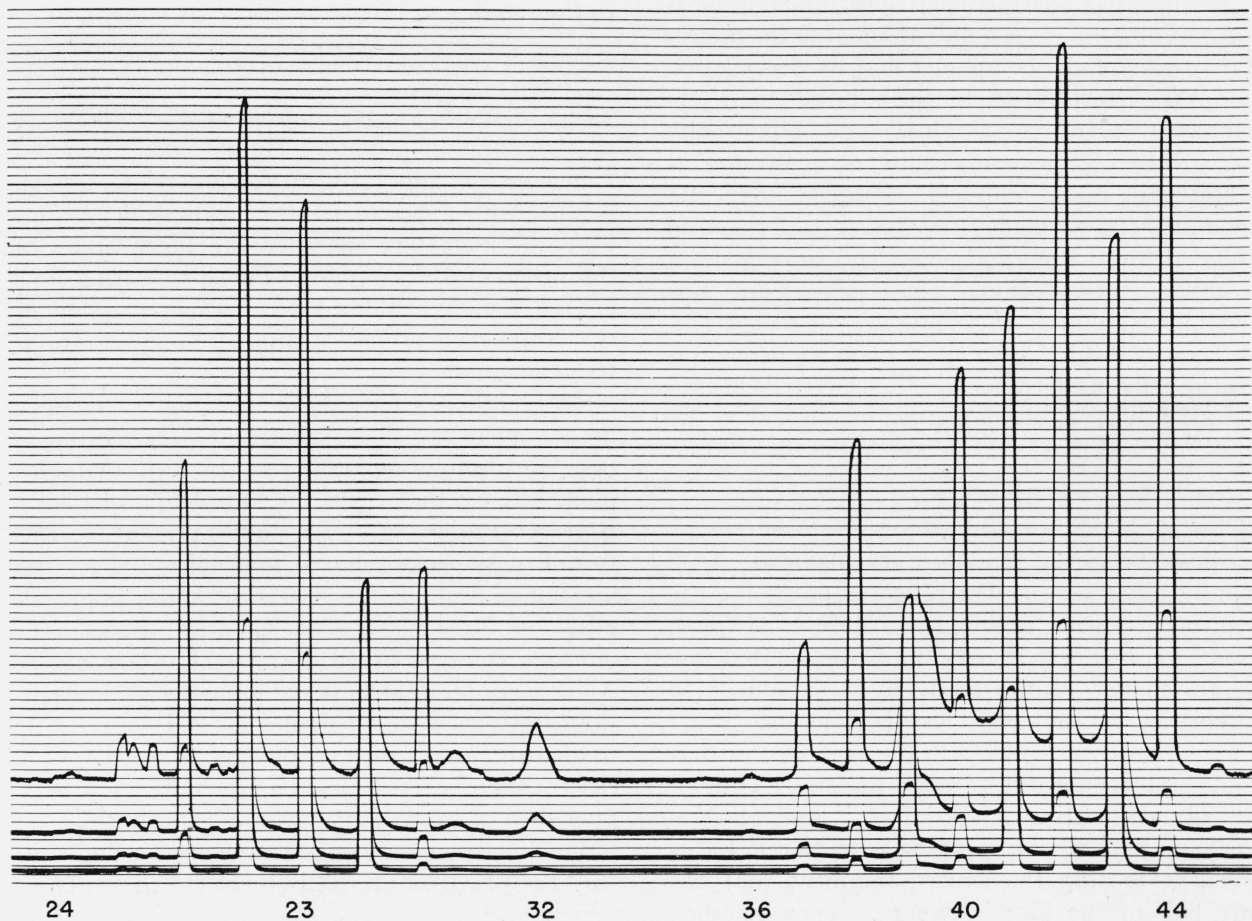

FIGURE 1. *Part of n-butane mass spectrum showing metastable transition peaks at mass numbers 25.1, 30.4, 31.9, and 39.2 and smaller peaks at 24.1 and 37.1.*

eter traces in decreasing order of sensitivity from top to bottom. The 43 peak is the maximum peak. There are four conspicuous metastable transition peaks in this range (25.1, 30.4, 31.9, and 39.2) and three other small ones (24.1, 35.1, and 37.1) that require careful measurement and comparison with other spectra for their verification. The peak at 31.9 is a good example of the characteristic appearance of these peaks. It is about three times the normal peak width. The peak at 39.2 is the largest of these, but it is incompletely resolved from the large 39 peak so that the value of the peak height is more uncertain than in the other cases.

This interference between normal peaks and metastable transition peaks occurs frequently and can give rise to a large uncertainty in the peak height. However, because of the abnormal width of the metastable transition peaks a rough estimate of peak height can often be made even when a small normal peak is exactly coincident with it. Hipple's analysis (see footnote 3) shows that the relative height of a metastable peak will depend on the draw-out potential, which is in this spectrometer a variable inversely proportional to the mass. It also depends on the resolving power of the spectrometer.

III. Intensity Relations

The relation (eq 1) between apparent mass and the initial and final masses is theoretically sufficient to determine both m_i and m_f, because there is the additional condition that m_f and m_i are integers equal to or less than the molecular weight. In practice, m_a is not always known with sufficient accuracy to give a unique answer. An important guiding principle has been the fact that wherever a metastable transition is observed m_f and m_i correspond to relatively large mass peaks in the mass spectrum.

We have looked for a quantitative intensity rule. The ratio R of the observed intensity at m_a to the product of the intensities at m_f and m_i,

$$R = I(m_a)/I(m_f) \times I(m_i), \qquad (3)$$

is usually of the order of magnitude 0.01 when I's are expressed on the basis of the maximum peak equal to unity. One would expect variations for instrumental reasons where different values of m_a are compared. There is, however, a nearly equal range of variation when one compares the same transition in different compounds. The average value of R for all observations is about 0.01, and this furnishes a criterion for estimating whether or not observable metastable peaks are to be expected. Metastable transition peaks very rarely exceed 1 percent of the maximum intensity, and this is consistent with the average value of R.

The identification of transitions has been aided by going systematically from simple to more complicated molecules in each series. In the saturated series, C_nH_{2n+2}, it is only the parent peak that is uniquely characteristic of the particular n value. The other peaks can also come from dissociation of heavier molecules. Correspondingly, metastable transitions keep recurring in successive members of the series except for cases where m_i is the parent mass.

IV. Results

The 362 metastable transitions observed in 55 compounds involve 32 different transitions insofar as initial and final masses are concerned. If the transitions are classified according to the neutral mass lost, there are 10 classes involving loss of mass 2, 15, 16, 26, 27, 28, 29, 30, 42, and 44, or H_2, CH_3, CH_4, C_2H_2, C_2H_3, C_2H_4, C_2H_5, C_2H_6, C_3H_6, and C_3H_8.

Loss of mass 2.—Loss of mass 2 is by far the most frequent type of transition. Eight different transitions involving loss of mass 2 are listed in table 1. The last metastable transition is unique insofar as relative intensity is concerned. The ratio of the peak at 110 to the product of the peak heights at 114 and 112 is 7.3. The average

TABLE 1. *Metastable transitions involving loss of mass 2*

Apparent mass	Initial mass	Final mass	Occurrence
24.1	28	26	Ethane, propane, n-butane, ethylene, butenes, butadienes, and butynes.
25.1	29	27	Saturated hydrocarbons C_2 to C_8, butenes and pentenes.
35.1	39	37	Butanes and mono-olefins C_3 to C_5, butadienes, and 1-butyne.
37.1	41	39	Saturated hydrocarbons C_4 to C_8 and propene, butenes, and pentenes.
39.2	43	41	Propane, butanes, 2 pentanes, hexanes, heptanes, octanes.
51.1	55	53	Pentenes.
26.1	30	28	Ethane (30 is parent ion).
110.0	114	112	2,5-Dimethylhexane (114 is parent ion).

value for this ratio is 0.01, and values exceeding 0.1 are very rare. The peak at 112 is very small in all other octanes so there is nothing unusual in the failure to observe a 110 peak in other cases. Figure 2 shows the 110, 112, and 114 peaks in 2,5-dimethylhexane.
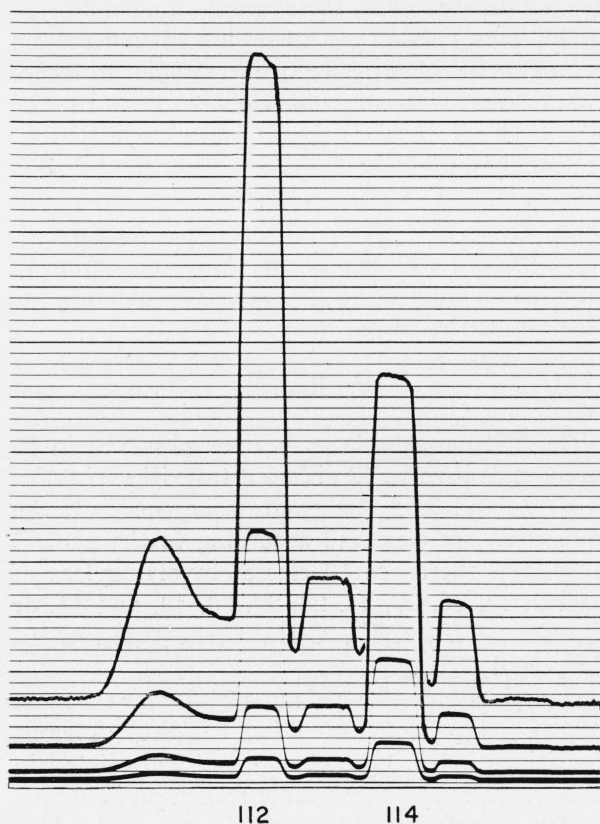

FIGURE 2. *Part of mass spectrum of 2,5-dimethylhexane showing the peak at 110 from the transition* $114^+ \rightarrow 112^+ + 2$.

Loss of mass 15.—Seven different transitions involving loss of CH_3 have been observed (see table 2). In all these cases the initial ion is the parent molecule ion. The first transition is of interest, because in 1,3-butadiene there are no CH_3 radicals, yet the metastable transition is very strong. In 1,2-butadiene there is a CH_3 radical but the 28.2 peak is not observed. According to the intensity rule, one would expect to find this peak in both butadienes as well as in the butynes. Similar transitions involving dissociation of the parent ion are found in all the butenes and pentenes. In the saturated hydrocarbons, there are only scattered instances of loss of 15 by the parent ion and in most of these cases it occurs with ab-

normally high intensity. In the heptanes and octanes the nonoccurrence of this transition in all the other isomers conforms to the intensity rule. Failure to observe a 58.6 peak in *n*-hexane is an exception to this rule. Except in *n*-butane there is a $(CH_3)_2CH$ group at one or both ends of the saturated molecules in all cases where this metastable transition occurs. Hipple, Fox, and Condon (see footnote 1) note that one might expect to find a transition $72^+ \rightarrow 57^+ + 15$ in *n*-pentane, but it is not observed.

TABLE 2.—*Metastable transitions involving loss of mass 15*

Apparent mass	Initial mass	Final mass	Occurrence
28.2	54	39	1,3-Butadiene and butynes.
30.0	56	41	Butenes.
43.2	70	55	Pentenes.
31.9	58	43	*n*-Butane (fig. 1).
58.6	86	71	2,3-Dimethylbutane.
72.3	100	85	2-Methylhexane.
86.0	114	99	2-Methylheptane and 2,5-dimethylhexane.

Loss of mass 16.—The loss of CH_4 from a hydrocarbon involves either a double dissociation or a rearrangement of hydrogen atoms in the initial ion before it dissociates. However, 35 cases of this have been observed in three different transitions listed in table 3. The 30.4 peak of *n*-butane is the only case involving a parent ion, and it occurs with abnormally high intensity. The nonoccurrence of 29.5 in one hexane, two heptanes, and two octanes is consistent with the intensity rule, as the product of the peak heights at 57^+ and 41^+ is small in these cases.

TABLE 3. *Metastable transitions involving loss of mass 16*

Apparent mass	Initial mass	Final mass	Occurrence
27.7	55	39	Pentenes.
29.5	57	41	Pentanes, 4 hexanes, 7 heptanes, and 16 octanes.
30.4	58	42	*n*-Butane (fig. 1).

Loss of mass 26.—The loss of C_2H_2 occurs in only one transition that is observed in 41 hydrocarbons:

$$m_a = 15.3 \qquad 55^+ \rightarrow 29^+ + 26.$$

This is found in all hexanes and octanes and all but one heptane and also in all butenes and pen-

tenes. Its occurrence conforms to the intensity rule.

Loss of mass 27.—Loss of C_2H_3 is observed in one transition from parent ions:

$$m_a=13.5 \qquad 54^+\rightarrow27^++27.$$

It occurs in both butadienes and in 2-butyne. It is abnormally weak according to the intensity rule. The unsymmetrical molecule 1-butyne does not show a 13.5 peak, although this peak is found in 1,2-butadiene, which is also unsymmetrical and requires a rearrangement of hydrogen atoms to break in half.

Loss of mass 28.—Loss of C_2H_4 appears in two transitions that recur in many saturated hydrocarbons:

$m_a=26.0 \qquad 71^+\rightarrow43^++28$ occurs in hexanes, 5 heptanes and 11 octanes.

$m_a=38.2 \qquad 85^+\rightarrow57^++28$ occurs in 5 heptanes and in 9 octanes. The appearance or nonappearance of these transitions in general conforms to the intensity rule.

Loss of mass 29.—Loss of C_2H_5 only occurs from parent ions and is observed in three transitions listed in table 4.

TABLE 4. *Metastable transitions involving loss of mass 29 from the parent ion*

Apparent mass	Initial mass	Final mass	Occurence
24.0	70	41	5 Pentenes.
50.4	100	71	n-Heptane.
63.4	114	85	n-Octane and 3,4-dimethylhexane.

Loss of mass 30.—Loss of C_2H_6 can only occur from a double dissociation or by a rearrangement. As the dissociating ion is always the parent ion, double dissociation is indicated. Table 5 lists the four transitions observed. The intensity of 61.9 relative to the product of the intensities at 114 and 84 is high in the octanes.

TABLE 5. *Metastable transitions involving loss of mass 30*

Apparent mass	Initial mass	Final mass	Occurence
24.5	72	42	n-Pentane.
36.5	86	56	n-Hexane.
49.0	100	70	5 Heptanes.
61.9	114	84	5 Octanes.

Loss of mass 42.—Loss of C_3H_6 occurs in two transitions in heptanes and octanes:

$m_a=21.7 \qquad 85^+\rightarrow43^++42$ in 8 heptanes and 11 octanes;

$m_a=32.8 \qquad 99^+\rightarrow57^++42$ in 17 octanes.

The occurrence of 21.7 conforms to the intensity rule, but the relative intensity of 32.8 is abnormally high.

Loss of mass 44.—A peak at mass 31.4 in three heptanes has been tentatively ascribed to the following transition:

$$m_a=31.4 \qquad 100^+\rightarrow56^++44.$$

It is observed in n-heptane, 2,4-dimethylpentane and 2,3-dimethylpentane. Its occurrence does not conform entirely to the intensity rule.

V. Summary

On the basis of momentum considerations, it is believed that the process of ionization by electron collision consists in removing an electron from the molecule, and that the molecule ion may be left in a highly excited state and subsequently dissociate into various fragments. Because of the fact that some of the dissociation processes occur with a time delay of the order of 10^{-6} second, we have direct experimental evidence as to the nature of the dissociation processes. The great variety of metastable transitions show that molecule ions may dissociate step by step (in all cases where the initial ion is not the parent ion) or by losing a rather large mass from the parent ion. It is natural to assume that loss of masses CH_3, C_2H_4, C_2H_5, and C_3H_6 involve a single dissociation process, insofar as these are natural units of the hydrocarbon molecule. On the other hand, loss of masses CH_4 and C_2H_6 necessarily involve more complicated processes, either double dissociation or a rearrangement of hydrogen atoms.

The generality of the relation that the intensity of the metastable transition depends on the intensity of the initial and final ion peaks is interesting and in some respects surprising. Consider transitions involving parent ions. Where the parent peaks are small, dissociation of the parent ions is most probable; yet, these are the cases where metastable transitions are not observed. This is not a paradox because long life of an excited state implies low probability of transition. Many

transitions must take place with "half lives" much less than 10^{-6} second.

Hipple (see footnote 3) has measured the half life of the two transitions from the parent ion in n-butane

$$58^+ \rightarrow 43^+ + 15,$$
$$58^+ \rightarrow 42^+ + 16,$$
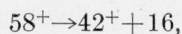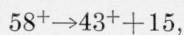
and estimated the fraction of 58^+ ions that are in the two initial states for these two transitions at time zero. The estimate is that roughly 9 percent of the 58^+ ions are in these two initial states. The 58^+ peak is 12.6 percent of the maximum peak and accounts for about 4 percent of all the ions in n-butane. If all are initially ions of mass 58, then 96 percent of the original ions dissociate with a very short life, 3.6 percent are stable or at least have a half life much longer than 10^{-6} second and 0.4 percent are in two states, each of half life about 2×10^{-6} second.

The nonoccurrence of a metastable transition involving loss of CH_2 is significant, for mass spectra indicate that loss of the structural unit CH_2 must be very frequent. It is concluded that the transition is always short lived.

The transitions involving loss of mass 2 are by far the most probable type of metastable transitions, and it is of interest that losses of mass 1 or mass 3 are never observed in hydrocarbons. Loss of mass 2 occurs in almost every case where there are two large peaks separated by two mass units with only a few exceptions. No such generalization can be made for loss of larger masses.

It follows from the intensity rule that isomers having similar normal mass spectra in general show the same metastable peaks. The occurrence of a peak at 28.2 in 1,3-butadiene and not in 1,2-butadiene is an exception to this. Dibeler, Wise, and Mohler [5] have found another exception among the isomers of monochloropropene. In general though, the metastable peaks will not be useful in chemical analysis of unknown mixtures for they merely reflect features of the normal spectrum.

The compilation of mass spectra and the identification of metastable transitions is continuing, and data will appear in the API catalog (see footnote 4).

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[5] V. H. Dibeler, C. E. Wise, and F. L. Mohler. Phys. Rev. **71**, 381 (1947).