

MassSpectrograph Study of the Ionization and Dissociation by Electron Impact of nOctane

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Mass-Spectrograph Study of the Ionization and Dissociation by Electron Impact of *n*-Octane

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A mass-spectrograph study of *n*-octane (C_8H_{18}) indicates that when bombarded by 120 e-volt electrons, it dissociates into a large number of small fragments, of which those containing two or three carbon atoms (and some hydrogen) are most numerous. Ions containing odd numbers of H

atoms are produced in larger quantities than those containing even numbers. The octane molecule displays a greater tendency to break up than does benzene (reported in a previous paper), which is in accordance with the reactions of these compounds in gaseous electrical discharges.

IN a recent article in *The Physical Review*¹ the writer reported an investigation of the ionization and dissociation of benzene (C_6H_6) by electron impact. The present paper deals with a similar study of *n*-octane (C_8H_{18}). These two compounds are representative of two important groups of hydrocarbons, the aromatics and the normal paraffins. The aromatic group, of which benzene is a member, is characterized by a molecular structure built up principally of units consisting of rings of six carbon atoms (the benzene ring). On the other hand, the normal paraffin molecule consists of a straight chain of carbon atoms. In each case, of course, the appropriate number of hydrogen atoms also are present.

These two classes of compounds have been found by Linder and Davis² to behave in quite different fashions in chemical processes taking place in electrical discharges. Aromatics tend

to polymerize, that is, the original molecules combine to form larger aggregates. This usually results in the formation of complex resins and waxes. There is not much breaking up of the original compound. However, paraffins behave in the opposite fashion. That is to say, there is considerable breaking up of the molecule and many compounds of molecular weight less than that of the original are formed. A larger part of the reaction products are gaseous, than in the case of an aromatic compound of similar molecular weight.

The mass-spectrograph studies of these two compounds carried out by the writer indicate that these characteristic modes of reaction may be attributed in a large part to the primary effect of electron bombardment rather than to succeeding secondary reactions. This follows since primary ions observed show that the benzene molecule tends to remain whole, whereas the octane molecule tends to break up immediately upon impact and without further collisions of any sort.

The data on *n*-octane are given in Fig. 1 and Table I. In Fig. 1 current through the magnet is plotted against electrometer deflection. The

* Formerly Detroit Edison Research Associate at Cornell University. The work reported in this article is a part of an investigation of the fundamentals of the disintegration of organic dielectrics being carried on at Cornell and supported financially by the Detroit Edison Company.

¹ Ernest G. Linder, *Phys. Rev.* **41**, 149 (1932).

² Linder and Davis, *J. Phys. Chem.* **35**, 3649 (1931).

eight groups of peaks correspond to ions having carbon atoms in number from one to eight. The large numeral over the group indicates the number of carbon atoms in the ions of that group, while the small numeral over the individual peaks in each group indicates the number

TABLE I. Ion group percentages for *n*-octane ($V=120$ volts).

Ion group	Pressure (mm Hg $\times 10^3$)					
	0.7	3.7	4.0	4.5	5.1	7.7
1C	1.2	0.5	1.5	2.5	0.9	1.2
2C	14.4	10.4	18.4	13.4	15.3	20.4
3C	34.8	31.5	29.7	35.1	35.6	28.2
4C	18.2	15.7	17.9	12.4	14.0	14.8
5C	8.4	11.3	9.6	7.8	9.7	10.5
6C	11.5	20.0	14.5	9.6	15.9	15.0
7C	3.7	2.0	1.1	1.3	0.0	0.7
8C	7.8	8.9	7.3	17.9	8.6	9.2

of hydrogens corresponding to that peak. For example, the highest peak in the figure has, according to the labels, the formula $C_3H_7^+$.

The peaks for H_2O^+ and OH^+ were prominent only in the runs made just after the apparatus was sealed to the pumps and exhausted. Water vapor is known to be very difficult to remove, especially when the apparatus is of a type that cannot be baked out, as in the present case. In making some of the runs the mercury pumps were run continuously for two weeks, and in this case the water peaks disappeared after about two days and could not be detected thereafter. Upon readmitting atmospheric air, again pumping out, and making a run, the water peaks reappeared.

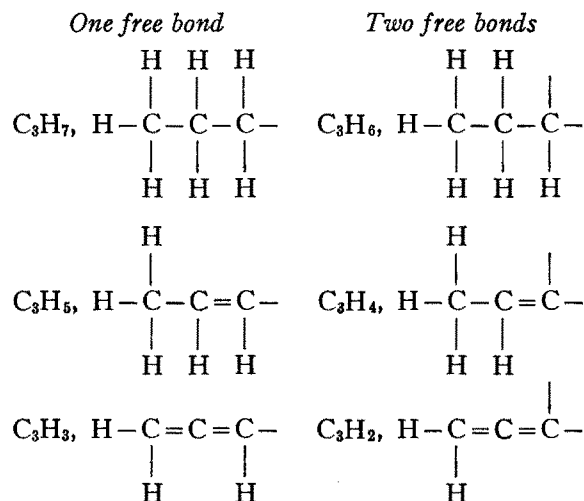
The small benzene peak likely arose from traces of that substance absorbed in the apparatus, especially in the waxes used in making some of the seals, and carried over from previous runs on benzene. This peak also disappeared, becoming undetectable after two days of pumping.

The octane was obtained from the Eastman Kodak Company. It was dried with sodium wire and distilled. Six fractions were taken. A part of the fourth fraction, which boiled in the range $124.4\text{--}124.8^\circ\text{C}$, was used for the mass-spectrograph work.

The most striking feature of the analysis of octane in comparison with that of benzene is the greater dissociation of the former into small fragments. In the case of benzene, the principal

ion was found to be a complete benzene molecule, but in the present case the principal ions are fragments having only two or three carbon atoms. This is in entire agreement with the reactions of paraffin and aromatic hydrocarbons in the glow discharge and Siemen's discharge.² It indicates that the large gas production of the paraffins is due at least in a large part to primary reactions in which the molecule is broken into fragments, which appear as gases or lighter liquids in the final products.

Another striking feature, exhibited by the 2C and 3C peaks, is the alternation of large and small peaks. In the 3C peak for example, the peaks of hydrogen content 1, 3, 5 and 7 are intense, whereas the 2, 4 and 6 are weak. This phenomenon was found not to vary with pressure and hence appears to be a primary effect. It would seem therefore that the hydrogen atoms tend to come off in pairs. It is worth noticing that the ions formed when the hydrogens thus come off have fewer free valence bonds than when they come off singly. This is made clear by the following diagram.



Obviously the ions having odd numbers of hydrogens, have only one free bond, whereas those having even numbers of hydrogens have two free bonds. The latter are probably the less stable, and according to the data are formed in fewer numbers, as should be expected.

Of course the structures given in the above diagram are not the only ones possible for those particular empirical formulas. Their only virtue

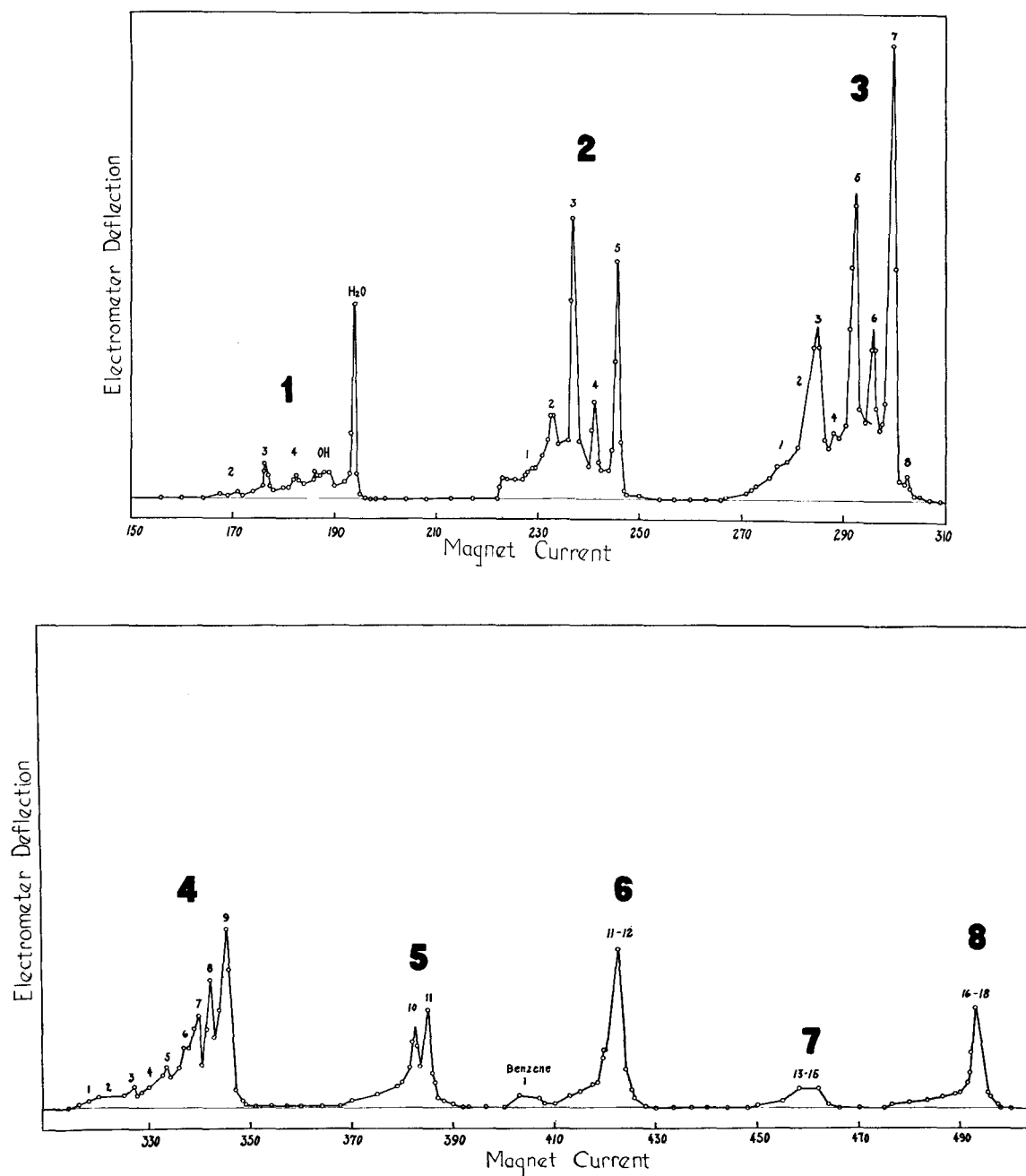


FIG. 1. The ions detected when *n*-octane is dissociated by electron impact. The large numerals give the numbers of carbon atoms and the small numerals the number of hydrogen atoms in the ions produced.

is that they permit an explanation of the variations in the peak heights.

The smallness and lack of structure of the peaks above $4C$ is rather surprising, and at first sight suggests that the result is spurious. Such an effect might occur due to differential absorption of these large ions in the magnet chamber. Their mean free path is of course shorter than that of the smaller ions and absorption should be greater for that reason. However, variation of the pressure produced no marked changes in the ratios of peak heights, as should be observed if differential absorption were playing a part. This can be seen from Table I, wherein ion percentages are given for various pressures.

The pressures listed are those in the ionization chamber, but the pressure in the magnet chamber, although much smaller, of course varies simultaneously with the other.

It should be borne in mind that the mass scale in Fig. 1 is not linear and that the peaks corresponding to heavy ions therefore are not actually as small in width as they appear. This non-linearity is corrected for in the data of Table I, and the percentages given there are true ion percentages.

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