Mass-Spectrograph Study of the Ionization and Dissociation by Electron Impact of Benzene and Carbon Bisulfide

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Benzene (C_6H_6) and carbon bisulfide (CS_2) have been analyzed by a mass-spectrograph designed especially for use with large molecules. In the case of benzene, ions have been found containing carbon in amounts from C_1 to C_6 with various amounts of hydrogen attached. The principal ion for electrons of 120 e-volts is $C_6H_6^+$. No negative ions and no H^+ ions were detected. Impacts of positive ions in the ionization chamber detach H atoms from the carbon ring, but the carbon content of all observed ions seems to be unaffected by such collisions. The carbon-to-carbon bonds appear to be more stable than in the straight-chain hydrocarbons. Carbon bisulfide was used principally to calibrate the mass scale, and no extensive work done on it. At a pressure of 9.7×10^{-3} mm Hg and impacts of 120 e-volts, the ions observed were CS_2^+, CS^+, S^+, and C^+.

THE only work which appears to have been done with the mass-spectrograph on large hydrocarbon molecules is that of Stewart and Olson,[1] who studied the straight-chain paraffins, propane (C_3H_8) and butane (C_4H_{10}). The present work on benzene (C_6H_6) was undertaken for the purpose of determining the behavior of a typical member of another important class of hydrocarbons, the aromatics, which are built up of rings of six carbon atoms, instead of straight chains, and therefore might be expected to exhibit a different sort of behavior in regard to dissociation by electron impact. The question was of interest to the writer in connection with studies of chemical reactions in electrical discharges, and that particular application of the data will be published in some chemical journal.

Apparatus and Procedure

Large molecules introduce additional difficulties to mass-spectrograph technique. High resolving power at large molecular weights is necessary, which requires the use of strong electric and magnetic fields, and slits as narrow as possible. The intensity is usually low because of the narrowness of the slits, and also because the ions are spread out over a large number of peaks. Furthermore, thermal dissociation at the filament must be eliminated, this problem being more acute with large molecules since they are in general more readily decomposed by heat.

Mass-spectrographs designed to eliminate thermal effects have been described by Stewart and Olson,[1] and Smyth and Stueckelberg.[2] In both these

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[1] Stewart and Olson, J.A.C.S. **53**, 1236 (1931).

[2] Smyth and Stueckelberg, Phys. Rev. **36**, 472 (1930).

apparatuses differential pumping was employed, the gas to be analyzed being introduced into the ionization chamber through a capillary and pumped out through two narrow slits, one opening into the magnet chamber and the other into the filament chamber. High speed pumps kept the pressures in these latter two chambers extremely low. Thus high pressure gradients at the slits were maintained, against which it seems very unlikely that any dissociation products formed at the filament could diffuse back into the ionization chamber. Thermal effects were decreased also by the use of low temperature, oxide-coated filaments.

Stewart and Olson give data indicating that thermal dissociation products were thus eliminated from the ionization chamber of their apparatus. The writer's mass-spectrograph was closely modelled after theirs, and the slit dimensions and pressure ranges employed were the same. It is therefore unlikely that thermal dissociation has appreciably affected the data given here. The similarity of the two apparatuses also renders comparison between the results more reliable.

For all of the data reported here a potential of 53 volts was used for drawing the ions out of the ionization chamber, the accelerating potential was about 515 volts. The radius of the ion path in the magnet chamber was 6.95 cm. The pressure in the magnet chamber was of the order of 10^{-5} mm Hg, while that in the ionization chamber was varied over the range from 10^{-3} to 80×10^{-3} mm Hg. This latter variation was effected, sometimes by changing the size of the capillary through which the gas was admitted, and sometimes by placing cooling baths of different temperatures around the bulb of liquid from which the vapor was drawn.

The benzene was purified as follows. Kahlbaum's thiophene free benzene was shaken six times with concentrated sulfuric acid. It was then washed with concentrated sodium hydroxide, with dilute sodium hydroxide, and finally with water until the wash water was neutral to litmus. It was dried over metallic sodium for 48 hours, and then distilled from the sodium. Then it was distilled three times, the middle fraction being taken each time. After being placed in the mass-spectrograph it was distilled twice in vacuum to remove dissolved gases. The carbon bisulfide used was Eimer and Amend's C. P. It was not treated in any manner before use.

In making the runs, the magnetic field was varied rather than the accelerating potential, on account of the unusually great mass range to be explored. The procedure was followed of starting with zero magnetic field and going up to the maximum necessary without reversals. This was done in order to get a more uniform mass scale. Reversals would introduce irregularities due to hysteresis and residual magnetism. At best however, it was found extremely difficult to avoid small accidental reversals due principally to heating of the rheostats and magnet coils. The field also appeared to vary appreciably with the temperature of the magnet core. Hence in general, the mass scale is not quite uniform. However all uncertainty in regard to the masses corresponding to the great majority of the peaks is removed by the calibration of the scale by means of the carbon bisulfide peaks.

Data and Discussion

A typical curve showing the various ions found is given in Fig. 1. For this run the energy of the impacting electrons was 120 e-volts, the pressure in the ionization chamber was 3×10^{-3} mm Hg, and that in the magnet chamber, 2.7×10^{-3}. Each peak is labeled with the formula of the ion to which it corresponds. No negative ions and no H^+ ions were observed, in agreement with the results of Stewart and Olson[1] on propane and butane, and that of Hogness and Kvalnes[3] on methane.

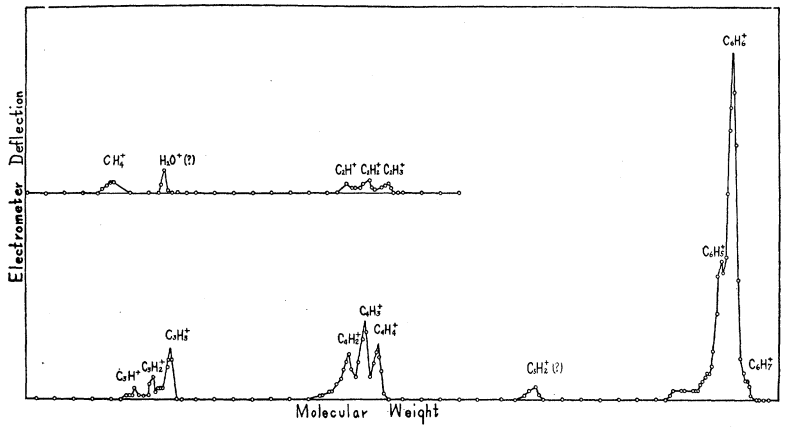

Fig. 1. Ions formed in benzene (C_6H_6) by 120 e-volt electrons.

In Table I is given the variation of ion percentage with pressure in the ionization chamber. A considerable number of runs were made in which measurements were taken only on the three largest groups of ions, i.e., the

Table I. *Percentages of ion groups formed by electron impacts in benzene at various pressures.*

Ion Group	Pressure (mm Hg$\times10^3$)			
	3.0	3.8	4.3	31.0
6C	71.5%	85.2%	57.0%	58.7%
5C	1.9	1.0	4.8	6.8
4C	16.1	9.9	21.6	23.7
3C	6.5	3.9	7.4	7.0
2C	3.3	0.0	4.4	1.8
1C	0.7	0.0	4.8	2.0

6C, 4C and 3C groups. The ion percentages for these three groups only (on the basis of 100 percent for the three groups only) are plotted in Fig. 2. These ion percentages were all determined by measuring the areas under the peaks with a planimeter, and correcting for the nonlinearity of the mass scale.

The scattering of the points in Fig. 2 is due principally to the difficulty of maintaining constant experimental conditions during the approximately two-hour period required to explore the large mass range. In spite of this scatter-

[3] Hogness and Kvalness, Phys. Rev. **32**, 942 (1929).

ing it is quite evident that the carbon content of these ions does not vary markedly with pressure. Likewise the hydrogen content was found not to vary, with the exception of the 6C group.

The variation of the shape of the 6C group with pressure is shown in Fig. 3. It will be observed that the structure on the left side of the peak increases with increasing pressure. This indicates that impacts made by the ions in the ionization chamber cause H atoms to be stripped from the carbon ring. The small peak corresponding to the molecular weight 79, which appeared in all the runs, is likely due to the attachment of a hydrogen atom to the $C_6H_6^+$ ion.

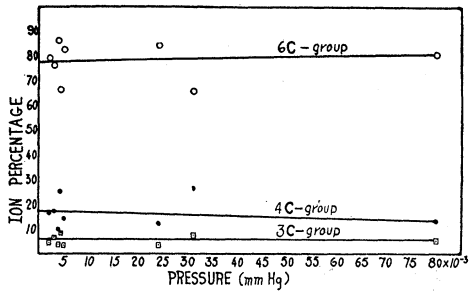

Fig. 2. Variation of ion percentage with pressure for benzene.

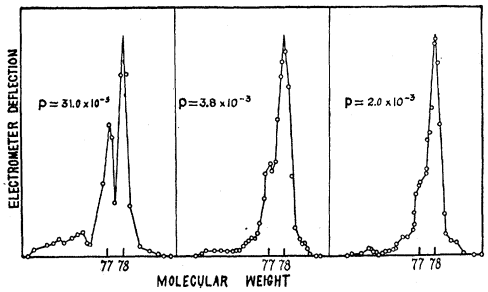

Fig. 3. Variation of 6C peak shape with pressure.

Attempts to determine critical potentials were unsuccessful due to low intensity. All that can definitely be concluded is that the appearance potential for the 6C peak is less than 40 volts.

In contradistinction to the results of Stewart and Olson[1] on normal paraffin hydrocarbons, the principal ion for benzene is a complete benzene molecule. For the paraffins, these authors found a very extensive dissociation into almost all possible lighter hydrocarbons, the ion corresponding to the entire original molecule being but a small percent of the total ions formed. Unfortunately they do not state the impacting energy of their electrons, but preliminary results of the writer's on octane, another straight-chain hydrocarbon, with 120 e-volt electrons, also show this extensive breaking up of the molecule. Thus it appears that straight carbon chains break up under electron bombardment more readily than does the six carbon ring.

This stability of the benzene ring may be partially due to the fact that in

order to divide a ring into two parts it is necessary to break it in *two* places, whereas to divide a straight chain into two portions it is necessary to break it in only *one* place. However the stability of benzene is doubtlessly due to other factors than this, since there are other six carbon ring compounds, e.g., cyclohexane, which are known from chemical evidence not to be nearly so stable as benzene.

A similar stability of the benzene ring in comparison with the paraffins has long been known in chemical reactions induced by heat,[4] and in various types of electrical discharges.[5] The reactions of benzene induced by these agents consist principally of polymerization and condensation, i.e., of the building up of more complex compounds by the adding together of benzene ring units with or without the evolution of a small amount of hydrogen. On the other hand, it is known that the normal paraffins under similar experi-

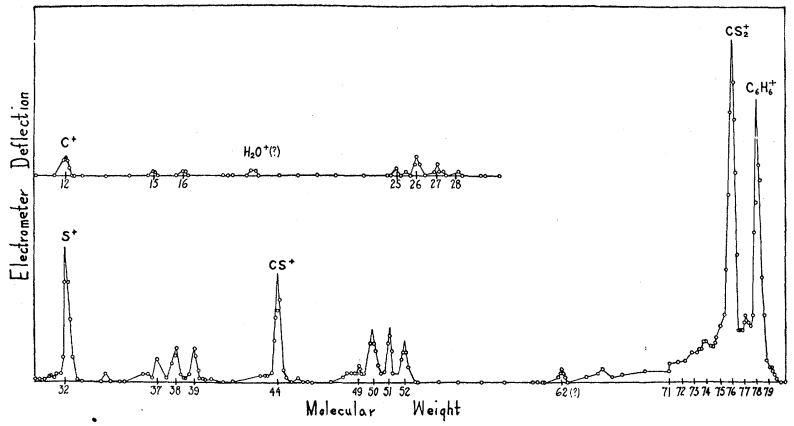

Fig. 4. Ions formed in a mixture of benzene and carbon bisulfide by 120 e-volt electrons.

mental circumstances suffer much more dissociation, and a much larger portion of the products are of a gaseous nature than in the case of benzene; see, for example, the work of Linder and Davis.[5]

The purpose of the runs with carbon bisulfide was to calibrate the mass scale and thus indentify the benzene peaks. However, since this compound seems not to have been investigated previously the data are of interest in themselves. The peaks observed are shown in Fig. 4 along with the benzene peaks. For this run the pressure was 9.7×10^{-3} mm Hg. The principal ion is CS_2^+, but peaks for S^+, CS^+, and C^+ are also present.

In conclusion the author wishes to express his thanks to the Cornell Physics Department for the laboratory facilities provided, and to Professor Vladimir Karapetoff, who is in general charge of the above-mentioned research program on dielectrics. He wishes especially to acknowledge his indebtedness to the President of the Detroit Edison Company, Mr. Alex Dow, and the Chief of Research, Mr. C. F. Hirshfeld, for the financial support of the above work and for permission to publish the results.

[4] Hurd, Pyrolysis of Carbon Compounds, Amer. Chem. Soc. Monograph No. 50.

[5] Linder and Davis, Jour. Phys. Chem. **35**, 3649 (1931).