another, but the number of overlying steps is very many less than for those which represent the species of even atomic weight.

5. Attention is called to a periodicity of 2 in the number of nuclear negative electrons, and a somewhat less prominent periodicity of 2 in the number of protons. In both of these, *even numbers give predominance over odd numbers in both number of species and in their abundance.*

6. Attention is called also to a periodicity of 2 in the relative negativeness (N/P) of the nucleus.

7. It is found that for constant *even* isotopic number the general difference between adjacent atomic species is 1 α-particle, or p_4e_2. For *odd* isotopic number (and atomic weight) the most common difference is $^1/_2$ α-particle, or p_2e, although the difference of a whole α-particle often occurs, also. Hypotheses concerning these relations are discussed.

8. Fig. 1 predicts the existence of a considerable number of hitherto undiscovered atomic species (isotopes) (consult note to Fig. 1).

9. Of the 19 elements of even atomic number for which in each case the most abundant isotope is known, the atomic weight and the isotopic number are both divisible by 4 in all but three instances. This periodicity is made apparent in the figure by using specially heavy horizontal lines for isotopic numbers divisible by 4.

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[Contribution from the Chemical Laboratory of McGill University]

UNSATURATION AND MOLECULAR COMPOUND FORMATION. III

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The present paper deals with the tendency of hydrocarbons to form molecular compounds, and a brief outline of previous work and contemporary views may serve as an introduction. The formation of a molecular compound results from the attractive forces between the molecules. These attractive forces in turn must result from particular atoms or groupings of atoms in the respective molecules. Thus the hydrates owe their origin to the residual valence of the oxygen atom which, not being completely compensated by 2 hydrogen atoms, gives to the water molecule a resultant attractive force which may come into play in combining with other molecules. Oxonium compounds also may owe their existence to the residual valence of the oxygen atom. Carbon, on the other hand, is almost completely satisfied by 4 hydrogen atoms, the resultant molecule having a small residual field of force as indicated by melting point, surface tension, and other physical properties: hence, hydrocarbons should show little or no tendency to form molecular compounds. Opposed to this, however, are experimental results which show that certain hydrocarbons do form molecular compounds.[1]

The hydrocarbons involved were unsaturated, and it might be supposed that, because of this unsaturation, the carbon atoms have their fields of force incompletely neutralized. Hence, these hydrocarbon molecules owe their attractive forces to the unsaturation. That this explanation is inadequate is brought out when the systems so far examined are considered. Thus, although allylene, toluene, *o*-, *m*-, and *p*-xylene, ethyl benzene, propyl benzene and propylene were shown to form compounds with hydrogen bromide, the equally unsaturated acetylene and benzene were shown not to form such compounds. To account for this the possible explanation was put forward that the tendency toward molecular compound formation is partly due to the unsaturation and is most pronounced in those molecules which do not have a symmetrical structure. In this paper a number of additional aromatic and one saturated hydrocarbon system are discussed, and somewhat more conclusive ideas suggested in view of the more extended data made available by the experiments to be described.

The additional hydrocarbon systems examined were *o*-, *m*-, and *p*-xylene, propyl benzene and methyl-cyclohexane, hydrogen bromide being the second component in each case. The method of investigation was the usual one of determining the freezing-point curves of the systems. If n invariant points are formed in such a system, this indicates the formation of $(n - 1)$ compounds.

The hydrocarbons, of highest obtainable purity, were allowed to stand over sodium for some time and then distilled; the proper fractions were retained for use. The freezing points were determined and the purities thus checked by comparison with the values found in the literature. The methyl-cyclohexane was prepared by the hydrogenation of toluene. The method as described by Sabatier[2] was followed with slight modifications. The furnace was made of Pyrex glass, the heating coil being of Nichrome wire, and all connections were glass-sealed so that in no part did rubber come in contact with the toluene or any of the reaction products. The product obtained on the first passage of the toluene vapor over the catalyst was passed a second time through the furnace in order to obtain more complete hydrogenation. This reaction product was nitrated repeatedly and the nitration products removed until the remainder was not acted upon in the slightest by the mixed acid. This was washed with water and sulfuric acid, and then subjected to fractional distillation. The fraction of lowest boiling point (101° to 101.2°) was chosen and the molecular weight determined in benzene. The values 99.2 and 99.5 were obtained at concentrations 5.4% and 12.7% as compared to 98.1, the theoretical value. This showed that little or no unhydrogenated toluene was present, and that the hexahydrotoluene is unassociated in benzene, as one would expect.

The hydrogen bromide was prepared and purified by fractional distillation over phosphorus pentoxide in the usual manner.

The temperatures were measured by means of a platinum resistance thermometer.

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[1] THIS JOURNAL, (a) **40,** 1561 (1918); (b) **43,** 1227 (1921).

[2] Sabatier, "Catalysis in Organic Chemistry," D. van Nostrand Co., **1922.**

The systems, propyl benzene, *o*-xylene, *m*-xylene, and methyl-cyclohexane were determined in the usual manner. The thermometer was directly immersed in a mixture of known composition made up by adding weighed quantities of the hydrocarbon to a weighed quantity of the hydrogen bromide. The liquid was cooled by a mixture of liquid air[3] or carbon dioxide and ether until crystals formed. The temperature was gradually allowed to rise, with vigorous stirring, until the last crystal just disappeared.

The system, *p*-xylene-hydrogen bromide could not be examined in this way on account of the high melting point of the *p*-xylene. A bulb method, previously described,[1a] was resorted to.

TABLE I

CONCENTRATIONS AND FREEZING POINTS

Hydrocarbon Mol. %	F. p. −°C.	Hydrocarbon Mol. %	F. p. −°C.	Hydrocarbon Mol. %	F. p. −°C.	Hydrocarbon Mol. %	F. p. −°C.
Ortho-xylene—Hydrogen bromide							
0.0	86.0	28.1	91.0	52.3	65.5	79.0	47.5
3.1	92.0	30.8	89.1	55.3	64.5	83.7	45.5
6.6	96.5	34.7	85.7	58.3	61.5	87.3	44.0
12.1	111.0	38.0	83.6	62.2	57.5	91.4	42.0
14.9	114.0	42.7	76.2	65.2	56.0	95.8	40.0
19.0	107.0	46.0	74.5	69.5	52.5	100.0	38.5
25.3	96.5	49.3	68.5	73.8	48.5		
Meta-xylene—Hydrogen bromide							
0.0	86.0	41.8	79.0	53.1	73.5	75.5	58.4
13.1	111.1	43.5	78.2	54.8	72.7	81.4	56.4
24.8	88.6	44.8	77.7	58.0	68.8	86.9	54.9
27.6	86.9	48.1	77.5	63.8	65.0	100.0	54.0
35.6	83.7	49.3	77.6	66.7	63.2		
36.9	80.8	51.8	75.5	71.0	60.9		
Para-xylene—Hydrogen bromide							
0.0	86.0	25.5	62.1	52.0	15.9	86.5	+9.4
4.5	93.5	31.1	48.6	54.7	13.8	92.3	+11.5
7.0	97.1	34.8	41.1	56.9	10.8	100.0	+15.0
10.6	101.4	43.5	26.0	69.5	1.5		
20.3	76.8	48.2	20.8	82.0	+5.7		
Propyl benzene—Hydrogen bromide							
0.0	86.0	19.4	119.4	38.1	107.4	62.6	110.3
2.1	88.3	23.2	116.8	41.6	106.1	65.5	113.4
4.5	92.6	25.2	115.4	46.2	105.2	100.0	145.0
8.0	97.9	27.9	114.4	50.1	105.4		
12.0	107.8	31.5	113.5	54.3	105.9		
15.8	119.1	35.3	109.3	58.5	106.5		
Methyl-cyclohexane—Hydrogen bromide							
0.0	86.0	10.1	93.9	28.8	101.9	49.9	110.0
2.0	87.9	13.0	95.0	32.6	103.4	54.2	111.8
4.0	89.9	15.6	96.3	37.5	105.3	59.7	113.8
6.0	91.4	19.6	97.8	40.8	106.6	100.0	124.5
7.9	92.5	25.2	100.4	43.4	107.6		

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[3] THIS JOURNAL, **43**, 1099 (1921).

In Table I the concentrations in molecular percentages and the freezing-points in minus Centigrade degrees are given.

The freezing-point curves of all the aromatic hydrocarbons which have been examined so far, with hydrogen bromide as the second component, are drawn on the accompanying diagram. The values for Curves I, II, VI and VIII have been taken from previous papers. In the latter, percentages were given by weight and were converted into molecular percentages by means of the formula

$$\text{Mole }\% = \frac{M_b\, Y}{100 M_a - Y\,(M_a - M_b)}$$

where M_a is the molecular weight of hydrocarbon, M_b the molecular weight of hydrogen bromide, and Y the percentage by weight of hydrocarbon.

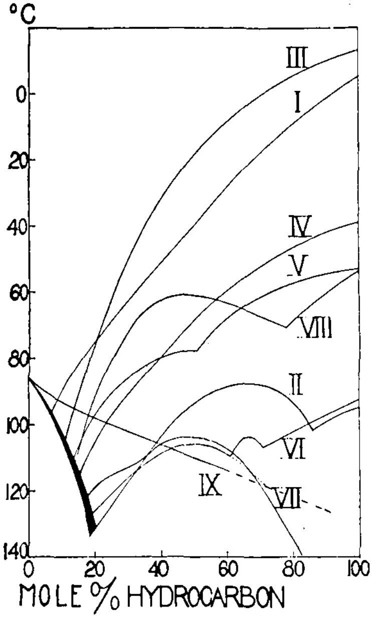

Fig. 1.—Freezing-point curves. I. Benzene. II. Ethyl benzene. III. *p*-Xylene. IV. *o*-Xylene. V. *m*-Xylene. VI. Toluene. VII. Propyl benzene. VIII. Mesitylene. IX. Methyl-cyclohexane.

Considering the curves in the order of the melting points of the pure hydrocarbons (excepting for the moment methyl-cyclohexane), and commencing with *p*-xylene, which has the highest melting point of all, it is seen that there is no compound formation. The same applies to benzene and *o*-xylene. With *m*-xylene, there is the first definite evidence of a compound having been formed with hydrogen bromide. As the melting points of the hydrocarbons diminish, the molecular compound formation becomes more and more pronounced, as evidenced by the nature of the curves. Thus, propyl benzene with the lowest melting point gives the compound of greatest stability.

The deductions which may be tentatively made are that the benzene nucleus, whether in benzene or its alkyl substitution products, has an outer field of force which has a definite tendency to attract hydrogen bromide molecules; this, however, can only come into play when this secondary valence is not of such a nature as to attract the molecules of its own species. The more symmetrical the molecule (such as *p*-xylene, benzene) the greater is the attraction of the molecules for each other; this results in the phenomenon of a relatively smaller attraction for molecules of hydrogen bromide.

Thus, if one considers a 50% molecular mixture of hydrocarbon and hydrogen bromide, when the temperature is lowered until crystals form, the latter will consist of the pure hydrocarbons, of a compound of the hydrocarbon and hydrogen bromide, or of pure hydrogen bromide, according to which of the forces of attraction (between molecules of (1) hydrocarbon and hydrocarbon, (2) hydrocarbon and hydrogen bromide, (3) hydrogen bromide and hydrogen bromide) is relatively the greatest.

Hydrogen bromide is present in all the systems and Attraction 3 may be looked upon as being small. Force 2 may be considered as comparatively independent of the hydrocarbon as long as the benzene nucleus is present. Force 1 varies considerably from hydrocarbon to hydrocarbon and, therefore, the nature of the crystal will be governed by whether Force 1 or 2 predominates. It is well known that the melting point may be considered to be a criterion of the magnitude of Force 1. In Curves III, I and IV, Fig. 1, this is so large that pure hydrocarbon is the solid phase, while in the other systems this attractive force of the hydrocarbon molecules for each other is diminished to such an extent as to allow the formation of molecular compounds which then form the solid phase.

Therefore, the unsaturation of the benzene nucleus may be looked upon as giving an external field which is partly neutralized by that of the hydrogen bromide molecule and when molecular compounds do not form, it is due to the greater attraction of the hydrocarbon molecules for each other.

That the attraction between hydrogen bromide molecules and aromatic hydrocarbon molecules is due to the unsaturation of the hydrocarbon molecule can be tested in a striking manner by choosing a hydrogenated aromatic hydrocarbon. The choice of such a compound, to prove anything, must be confined to one having a melting point equal to or lower than that of an aromatic hydrocarbon which will form a molecular compound with hydrogen bromide. Methyl-cyclohexane answers this requirement. Its freezing point is —124.5°, even lower than that of toluene in spite of its higher molecular weight, thus showing that the attraction between the methyl-cyclohexane molecules is less than the attraction of toluene molecules for one another. If any attraction between the hydrocarbon and hydrogen bromide molecules exists, other than that due to unsaturation, it should come into play to a greater extent in the case of methyl-cyclohexane than in the case of toluene. Therefore, the system, methyl-cyclohexane-hydrogen bromide, should show the existence of a molecular compound as stable at least as that found in the system, toluene-hydrogen bromide. It was with this in view that the methyl-cyclohexane system was examined. Curve IX shows that no molecular compound exists. Further evidence that with the disappearance of unsaturation, attraction between the hydrogenated toluene and hydrogen bromide disappears, is shown by that portion of the curve where hydrogen bromide is the solid phase. In all the other systems the portions of the curve where hydrogen bromide is the solid phase are identical, as they should be, provided no association of the hydrocarbon molecules occurs. Methylcyclohexane shows distinctly that in hydrogen bromide it is associated. The slope of the curve shows this to be the case. With increased concentration of hydrocarbon the slope diminishes.[4] Hence, with the disappearance of unsaturation the attraction between the hydrocarbon and the hydrogen bromide molecules disappears.

It is of interest to point out that the chemical behavior of aromatic hydrocarbons is in agreement with their chemical activities, particularly where reactions with acids are involved. A chemical reaction may be considered to take place in two stages, the first of which consists of the formation of a complex due to the molecular attraction between the reacting molecules, with subsequent interatomic changes. Thus it is found that on the agitation of a mixture of *o*-, and *p*-xylenes, with concd. sulfuric acid, the sulfonic acid of the *ortho* compound is obtained, but the *para* remains unchanged. A similar comparison of the chemical activity of benzene and its homologs, toluene, ethyl benzene, and propyl benzene, shows that the benzene is relatively inert and the others increase in activity in the order mentioned. That is, the chemical activity is in the same order as the tendency toward molecular compound formation.

Summary

The systems *o*-, *m*-, and *p*-xylene, propyl benzene and methyl-cyclohexane, with hydrogen bromide as second component, were examined, freezing points of molecular percentages of hydrocarbon, from 1 to 100, were determined, and molecular compounds shown to exist in the *m*-xylene and propyl benzene systems.

The formation of molecular compounds has been shown to be due to unsaturation. Failure to form a molecular compound in spite of unsaturation, is due to the relatively great attraction of the hydrocarbon molecules for one another.

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[4] These are analogous to the freezing-point curves of alcohol in water, for which no association takes place, and alcohol in benzene for which association of alcohol molecules does occur and gives a form to the curve similar to that of the methyl-cyclohexane-hydrogen bromide system. In the alcohol-water system the phenomenon is due to the great attraction between water and alcohol molecules, with the result that the alcohol does not associate. The attraction between alcohol and benzene molecules is small, and this enables the alcohol molecules to form complexes.