recrystallized from acetic ether. It melted at 124–125°. Thus the identification of this fraction with cadinene was confirmed.

From the results of this investigation, the following conclusion may be drawn:

The Formosan Hinoki wood oil consists chiefly of *d*-α-pinene and cadinene, with a small amount of oxygenated compounds. The amount of terpenes is about 70% and that of sesquiterpenes is about 24%.

Pinene hydrochloride may advantageously be purified by sublimation and it melts sharply at 132.5–133.5° (corr.).

TOKYO, JAPAN.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF VANDERBILT UNIVERSITY.]

ORGANIC MOLECULAR COMPOUNDS.

BY JAMES F. NORRIS.

Received December 23, 1915.

In a paper published sometime ago by Norris, Thomas, and Brown[1] it was shown that tetraphenylethylene dichloride, $(C_6H_5)_2CCl.ClC(C_6H_5)_2$, formed well-characterized molecular addition products with chloroform and with carbon tetrachloride. Since organic molecular compounds have been little investigated, it seemed advisable to study such compounds more fully in order to determine, if possible, the conditions necessary for their formation. It is evident that a satisfactory theory of valency must be susceptible of explaining the atomic relationships in molecular compounds; for these substances are as definite in their composition as the simpler compounds, which are explicable with our present inadequate views; and, moreover, certain so-called molecular compounds are known which are more stable than many possessing a simple atomic structure. Our present theories of valency, as applied to organic chemistry, do not cover the case of molecular compounds, and we cannot, therefore, predict what atomic conditions are necessary for the formation of a compound as the result of the union of two molecules. The field of organic chemistry is the best available for the investigation of these atomic conditions, since slight and graded changes in the combining power which holds the atoms together can be made by introducing into the molecule one or more groups the nature of which can be changed at will.

The results described below were obtained in a preliminary study of this problem. Work is actively in progress to determine, if possible, the causes that affect the mutual affinity between atoms in organic molecules, and the relationship between these affinities and the phenomenon of the formation of molecular compounds.

As has been emphasized of late, the bonds which unite atoms in an organic compound are markedly affected by the nature of the surround-

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[1] *Ber.*, 43, 2940 (1910).

ing atoms. For example, the union between the carbon atom and the chlorine atom in methyl chloride is quite different from that between the same elements in triphenylmethyl chloride. At present we have no absolute method of measuring this difference, and no way of representing it in our graphic formulas; but it is possible to get a definite conception of the relative activity of the corresponding atoms in a series of compounds of the same type. The results reported below have to do with the study of this problem from the standpoint of the formation of molecular compounds. It is not certain whether such substances are formed as the result of the existence of what might be called a molecular valency possessed by the two constituents of the compound, or whether the union is the result of the affinity residing on single atoms in each of the molecules. If the latter view be true, the atoms which are instrumental in forming the molecular compound possess in the simpler molecules a power of combination which comes into play when the union takes place. According to the accepted views, chloroform and carbon tetrachloride are saturated compounds, yet they are able to unite with other compounds. They possess, therefore, a power of combination which must be taken into account in an adequate theory of valency.

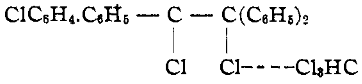
In order to guide the work undertaken to throw light on this question, a hypothesis was formulated and the deductions from it were tested. With our present conception of valency it seemed that more definite views susceptible of being tested could be arrived at by attributing the power of molecules to form compounds among themselves, to single atoms in these molecules. A working hypothesis was arrived at as the result of the following considerations: Every element contains a definite amount of chemical energy which undergoes transformation, in part, when it enters into combination with another element. The amount of chemical energy in the resulting compound is determined by the amount of energy transformed in its formation. This residual energy, which still is present in the atoms, makes it possible for the molecule to unite either with additional atoms, or with molecules to form molecular compounds. If, in the formation of the original molecule, a large share of the chemical energy is transformed, the resulting compound would have little power of union with other things; if, on the other hand, a small amount only of the chemical energy has been lost, the compound would exhibit in a marked degree the power to unite with other substances. If this residual energy is sufficient in amount, a compound with another element is possible, whereas if the amount is small a molecular compound may be formed. In general, the change in energy which takes place in the formation of molecular compounds is less than that transformed in the formation of simple compounds. For example, when phosphorus unites with chlorine to form phosphorus trichloride but a part of the available chemical energy is transformed into heat. When the trichloride unites with chlorine to form the pentachloride more of the energy is transformed, but the latter compound still possesses available chemical energy. It is not sufficient in amount to react with more chlorine, but it can become available when the molecule is brought into contact with other molecules; many molecular compounds containing phosphorus pentachloride are known. When we write the formula of the compound as PCl_5 and consider the molecule a saturated one, the conclusion is not in accord with the facts. When one phosphorus atom unites with five chlorine atoms but a part of the available energy of the chlorine atoms is transformed; they, therefore, possess energy which can come into play in the formation of molecular compounds. Many compounds which contain a number of chlorine atoms, such as $SbCl_5$, $AsCl_5$ and $SnCl_4$, form well-characterized molecular compounds with both inorganic and organic molecules. The above views are but a restatement of the electrochemical theory of Berzelius. It has often happened in the development of science that advance has come as a result of the application of the older theories to the facts which have been discovered since the enunciation of these theories. According to this view all compounds are probably unsaturated.

The application of this hypothesis in the case of tetraphenylethylene is as follows: The hydrocarbon, which has the formula $(C_6H_5)_2C = C(C_6H_5)_2$, exhibits an anomalous behavior; it will not form a dibromide when treated with bromine, and does not show the characteristic properties of an unsaturated compound. It is evident that the chemical affinity of the four phenyl groups almost completely "neutralizes" that possessed by the two carbon atoms. They do not contain enough available energy to permit of their union with bromine. It was shown that the hydrocarbon will unite with chlorine, however. In the resulting compound, tetraphenylethylene dichloride, the two chlorine atoms are very labile; they are removed easily by metals, and interact at room temperature with water. The two carbon atoms to which the chlorine atoms are attached do not hold the latter firmly, since they possessed but a small amount of available chemical energy which was transformed in the formation of tetraphenylethylene dichloride. As a result, according to the hypothesis put forward here, but a small amount of the chemical energy of the added chlorine has been expended in the union, and, as a consequence, a large share of it is left which can become available in the formation of molecular compounds. It is highly probable that if we could measure the heat of formation of tetraphenylethylene dichloride from the hydrocarbon and chlorine, we should find it much smaller in amount than the corresponding heat of formation of ethylene chloride. In the paper cited it was shown that tetraphenylethylene dichloride formed molecular compounds with chloroform and with carbon tetrachloride;

in this paper analogous addition products with bromoform, dichlorobromomethane, carbon tetrabromide, and sulfuryl chloride are described.

From the point of view which has been stated, it seemed probable that compounds which contained an active chlorine atom would possess the power to form molecular compounds. The activity of the chlorine atom in triphenylchloromethane, $(C_6H_5)_3CCl$, resembles that of the halogen atoms in tetraphenylethylene dichloride. Its activity can be traced to the same cause, namely, the fact that in establishing the union between the methane carbon atom and the halogen, but a small amount of chemical energy is transformed, and as a result, the chlorine atom in the chloride possesses a large share of its energy and is consequently active. In testing this view it was found that triphenylchloromethane forms molecular compounds with carbon tetrachloride and with acetone; other addition products are now being investigated. It is interesting to note in this connection that benzoyl chloride and analogous compounds which contain an active chlorine atom form molecular compounds; these, also, are now under investigation.

It has been shown by previous investigators that the ability to add bromine at the double bond in compounds of the type $R_2C = CR_2$ is markedly affected by the nature of the radicals joined to the ethylene carbon atoms. We have found that a number of compounds of this type which do not add bromine, form dichlorides. The ability of the latter to form molecular addition products is being studied. It has been found that *p*-chlorotetraphenylethylene unites with chlorine, and that the resulting dichloride forms molecular compounds with chloroform and carbon tetrachloride. The stability of these compounds is much less than that of the analogous addition products containing tetraphenylethylene dichloride. As was expected the compound containing carbon tetrachloride was the more stable; it contained two molecules of carbon tetrachloride. The chloroform addition product contained but one molecule of the added halogen compound. The introduction of chlorine into one of the benzene rings reduced the power of the resulting molecule to form addition products and made it unsymmetrical. The two ethylene carbon atoms do not possess the same degree of unsaturation, and, as a consequence, the chlorine atoms added to these might be expected to show different properties. It is highly probable that the formula for the chloroform addition product should be written thus:



$$\begin{array}{lllll} ClC_6H_4.C_6H_5 & — & C & — & C(C_6H_5)_2 \\ & & | & & | \\ & & Cl & & Cl\text{----}Cl_3HC \end{array}$$

to emphasize the fact that the halogen in one of the rings has weakened the power of one of the chlorine atoms to form molecular compounds. A study of tetrabromotetraphenylethylene dichloride brought out the interesting fact, which might have been foretold from the facts just stated, that the compound did not possess the power to form molecular compounds with any of the substances investigated.

From the results obtained and the hypothesis put forward, we were led to investigate the possibility of the formation of molecular addition products by compounds other than those containing halogen atoms. From the point of view put forward it appeared probable that substances of two distinct classes might possess the power to form molecular compounds. The first class consists of compounds which possess an active element or group. The fact that such an element or group can be readily removed by reagents indicates that one factor in its activity is that it is not firmly bound in the compound, or, in other words, it contains a large amount of available energy. A study of compounds of this type is now being made. It has been found, for example, that triphenylcarbinol, which contains an active hydroxyl group, forms molecular compounds with acetone and with carbon tetrachloride. It is of interest to point out in this connection that the methane hydrogen atom in triphenylmethane can be readily replaced by other atoms or groups; it is unusually active for a hydrogen atom joined to carbon. Triphenylmethane forms a well-characterized molecular compound with benzene, and it was shown by one of us[1] that it forms a compound with aluminium chloride. It is highly probable that the hydrogen atom joined to the methane carbon atom furnishes the chemical energy which is involved in the formation of such molecular compounds. The hydrocarbon is being further investigated from this point of view.

The second class of substances which might possess the power to form molecular compounds are those containing so-called unsaturated carbon atoms which have largely lost their power to add other atoms as the result of the accumulation of negative groups around the unsaturated atoms. As has been pointed out the unsaturation of tetraphenylethylene and similar compounds is very slight. The available energy is not great enough in amount in most cases to bring about the reactions characteristic of highly unsaturated compounds like ethylene. The unsaturation may be great enough, however, to lead to the formation of molecular compounds. In confirmation of this view it was found that tetrabromotetraphenylethylene, which contains an inactive double bond, forms molecular compounds with acetone, methylethyl ketone, diethyl ketone, ethyl acetate, carbon tetrachloride, and benzene. Other compounds of this type are being studied. It is of interest to note in this connection that benzene forms a number of molecular compounds. The power to form such compounds is due, according to the views put forward here, to the fact that the unsaturation of benzene is very slight; it resembles that of the double bond

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[1] *Am. Chem. J.*, 26, 499 (1901).

in tetraphenylethylene. The available energy is not sufficient in amount to permit the compound to add atoms readily, but is sufficient for the formation of molecular compounds, since in such formation small amounts of energy are, in general, transformed.

The views put forward have led to the conclusion that the number of atoms with which any atom unites is not limited to the valence of the latter. The tendency of atoms to lose their chemical energy is the factor which leads to the formation of compounds. This loss can be brought about in steps. The number of possible steps when atoms or radicals are added is the valence of the element. When, however, a smaller expenditure of energy takes place, as in the addition of molecules, the number of steps can be increased. It is highly probable that the forces which bind together molecules are of the same nature as that which comes into play in the formation of simple compounds; the difference is one not of kind but amount.

The existence of many of the organic molecular compounds described in the literature can be explained from the point of view put forward here. A large amount of additional work must be done, however, to test the hypothesis stated. This will include a study of the effect of the nature of the radicals present in a compound on its ability to form molecular addition products. Since decrease in temperature is often associated with increase in combining power, it is probable that, at temperatures lower than that of the atmosphere, such an increase may lead to the formation of molecular compounds by substances which do not ordinarily exhibit this power. A study of the effect of temperature on the formation of molecular compounds is accordingly being made.

Experimental Part.[1]

With KATHARINE E. ROONEY, JANET S. MURPHY and CAROLYN F. DODGE.

Preparation of Tetraphenylethylene Dichloride.—The tetraphenylethylene used throughout the work was prepared easily and in large quantities from benzophenone chloride and diphenylmethane according to the directions given in the paper referred to in the introduction. Directions for a convenient method of preparation of benzophenone chloride from carbon tetrachloride and benzene are also given in the same paper. In order to make tetraphenylethylene dichloride the hydrocarbon was dissolved in the smallest amount of chloroform and the solution was then saturated with dry chlorine. The solvent was next distilled off on a water bath, and the resulting crystals were recrystallized from a mixture of equal volumes of dry ethyl acetate and carbon bisulfide. The yield of the pure compound was about 90% of the theoretical. The compound forms large transparent crystals that melt at 160–162° with decomposition.

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[1] The work described in the paper was done in the laboratory of Simmons College.

Preparation of the Compound $(C_6H_5)_2CCl.ClC(C_6H_5)_2.2CHBr_3$.—A compound of tetraphenylethylene dichloride and chloroform was described in the paper referred to in the introduction. Experiments with bromoform led to the preparation of an analogous compound. This addition product was prepared by saturating hot bromoform with tetraphenylethylene dichloride, and allowing the solution to cool. The crystals were filtered off and after drying in the air were analyzed by determining the loss in weight (bromoform) when heated in a Victor Meyer bath containing boiling water, the temperature of the inside of the bath being 92°.

1.6235 g. came to const. wt. in 3 hrs. and lost 0.9052 g. Calcd. loss in wt. for the formula given above, 55.67%. Found, 55.75%.

The composition of the addition product was also determined by synthesis. A weighed quantity of tetraphenylethylene dichloride was placed in a desiccator with a vessel containing bromoform, and kept until the dichloride came to a constant weight. On account of the slight volatility of bromoform the addition took place very slowly; the weight was constant at the end of ten weeks. The tetraphenylethylene dichloride used was obtained by allowing the crystals of its addition product with chloroform to lose the latter at room temperature; it was in the form of a friable porous mass.

1.0733 g. of tetraphenylethylene dichloride increased in wt. 1.3467 g. Calc. for $(C_6H_5)_2CCl.ClC(C_6H_5)_2.2CHBr_3$: 125.6%. Found: 125.4%.

Preparation of the Compound $(C_6H_5)_2CCl.ClC(C_6H_5)_2.2CBr_4$.—A compound of tetraphenylethylene dichloride and carbon tetrachloride was described in the paper cited above. The addition product with carbon tetrabromide was prepared by dissolving the compound and tetraphenylethylene dichloride in carbon disulfide and allowing the solution to evaporate spontaneously. Solutions were prepared containing the constituents in the molecular ratio of one of the dichloride to one of carbon tetrabromide and of one of the former to two of the latter. The same compound was obtained in the two cases. It melted at 144–147°. The substance was analyzed by heating it to constant weight at 92° in a Victor Meyer bath.

1.3220 g. lost 0.8394 g. in 36 hrs. when heated to const. wt. Calc. for $(C_6H_5)_2CCl.ClC(C_6H_5)_2.2CBr_4$: 62.23%. Found: 63.42%.

Preparation of the Compound $(C_6H_5)_2CCl.ClC(C_6H_5)_2.2CHBrCl_2$.—The compound was prepared by crystallizing the dichloride from hot dichlorobromomethane. It resembled in appearance the analogous chloroform compound.

0.8677 g. lost 0.4165 g. in 1 hr. at 92°. Calc. for $(C_6H_5)_2CCl.ClC(C_6H_5)_2.2CHCl_2Br$: 44.87%. Found: 47.99%.

Preparation of the Compound $(C_6H_5)_2CCl.ClC(C_6H_5)_2.2SO_2Cl_2$.—This compound was prepared by crystallizing tetraphenylethylene dichloride from hot sulfuryl chloride. It was also formed by placing a sample of tetraphenylethylene chloride in a desiccator containing sulfuryl chloride. The compound crystallizes in shiny, transparent crystals, which effloresce rapidly and are readily decomposed by the moisture of the air. Analysis indicated that the formula was that given above although concordant results were not obtained on account of the instability of the compound.

Preparation of the Compound *p*-$ClC_6H_4.C_6H_5.CCl.ClC(C_6H_5)_2.CHCl_3$.—*p*-Chlorotetraphenylethylene was prepared as described in the article cited above. It was purified by the method described below. The compound was formed by boiling together as long as hydrogen chloride was evolved a mixture of *p*-chlorobenzophenone chloride and diphenylmethane. The product was distilled and the part which solidified was crystallized repeatedly from hot alcohol, and finally from glacial acetic acid, when it was obtained in small crystals which melted at 165–167°. The compound was dissolved in chloroform and the solution saturated with dry chlorine. On evaporation a gummy mass was obtained. When this was dissolved in acetone and the solution was allowed to evaporate, well-formed crystals of *p*-chlorotetraphenylethylene dichloride were obtained. The compound is readily soluble in chloroform, carbon tetrachloride, and petroleum ether; it dissolves with difficulty in cold acetone, and readily in hot acetone. It melts at 135–137°.

The addition product of *p*-chlorotetraphenylethylene dichloride and chloroform was prepared by saturating warm chloroform with the dichloride and cooling the resulting solution in a mixture of ice and concentrated hydrochloric acid. The product was obtained in shiny, cubical crystals resembling the analogous compound containing tetraphenylethylene. It melted at 58–59°. It loses chloroform rapidly in the air.

0.4643 g. lost 0.0869 g. at 92°. Calc. for $ClC_6H_4.C_6H_5.CCl.ClC(C_6H_5)_2.CHCl_3$: 21.42%. Found: 18.72%.

Preparation of the Compound $ClC_6H_4.C_6H_5.CCl.Cl(C_6H_5)_2.2CCl_4$.—The compound was prepared by crystallizing the dichloride from carbon tetrachloride. The crystals which separated on cooling melted at 91–93°. As the carbon tetrachloride was lost quickly in the air it was difficult to obtain a sample for analysis free from mechanically held solvent and at the same time prevent loss of the chemically combined carbon tetrachloride. The stability of this compound is markedly different from the one of analogous composition containing tetraphenylethylene dichloride.

0.5664 g. lost 0.257 g. at 92°. Calc. for $ClC_6H_4.C_6H_5.CCl.ClC(C_6H_5)_2.2CCl_4$: 42.7%. Found: 46.3%.

Preparation of the Compound *p*-$(BrC_6H_4)_2C = C(C_6H_4Br)_2$.—An improved method of preparing this compound is as follows: To 5 g. of tetraphenylethylene, which has been ground to a fine powder and is spread out in a thin layer, are added 7.5 cc. of bromine in small portions and with stirring. When the excess of bromine has evaporated, the product is crystallized from boiling acetone, in which it is not very soluble. It is obtained in shiny crystals which contain acetone (see below). When heated the acetone is lost and the compound then melts at 251–252°. The yield of the pure compound is about 65% of the theoretical.

Preparation of the Compound $(BrC_6H_4)_2CCl.ClC(C_6H_4Br)_2$.—The compound was prepared by saturating a solution of tetrabromotetraphenylethylene in carbon tetrachloride with dry chlorine. The solution is next evaporated to dryness and the residue crystallized from a hot mixture of equal volumes of carbon disulfide and ethyl acetate. The compound melts at 190–192°. Unsuccessful attempts were made to prepare addition products of the compound with chloroform and carbon tetrachloride.

Preparation of the Compound $(BrC_6H_4)_2C = C(C_6H_4Br)_2.2(CH_3)_2CO$.—Tetrabromotetraphenylethylene crystallizes from acetone in shiny needles which become opaque when allowed to stay in the air.

0.9642 g. of substance lost 0.1357 g. at 92°. Calc. for the formula given above: 15.09%. Found: 14.06%. Another sample which was allowed to stand 4 minutes in the air after all visible acetone had been removed lost 15.53% when heated to constant weight.

Preparation of the Compound $(BrC_6H_4)_2C = C(C_6H_4Br)_2.CH_3COC_2H_5$.—This compound was prepared by crystallizing the substituted hydrocarbon from methylethyl ketone. The molecular compound is much more stable than the acetone addition product.

0.7410 g. substance lost 0.0727 g. at 92°. Calc. for the formula given above: 10.00%. Found: 9.81%.

Preparation of the Compound $(BrC_6H_4)_2C = C(C_6H_4Br)_2.(C_2H_5)_2CO$.—The addition product was prepared by crystallizing the substituted hydrocarbon for diethyl ketone. It crystallizes in long, lustrous needles.

0.6806 g. of substance lost 0.0842 g. at 92°. Calc. for the above formula: 11.71%. Found: 12.37%.

Preparation of the Compound $(BrC_6H_4)_2C = C(C_6H_4Br)_2.CCl_4$.—This compound was formed when tetrabromotetraphenylethylene was crystallized from carbon tetrachloride. The compound forms small crystals which effloresce rapidly.

0.4421 g. lost 0.0803 g. Calc. for the above formula: 19.20%. Found: 18.17%.

Preparation of the Compound $(BrC_6H_4)_2C = C(C_6H_4Br)_2.CH_3COOC_2H_5$.—This compound, prepared by crystallization from ethyl acetate, was relatively stable. When a gram was exposed to the air at room temperature it lost ethyl acetate at the rate of one milligram in 10 minutes.

0.9032 g. lost 0.1105 g. at 92°. Calc. for the above formula: 11.96%. Found: 12.17%.

Preparation of the Compound $(BrC_6H_4)_2C = C(C_6H_4Br)_2.C_6H_6$.—The compound formed large, lustrous needles.

1.3694 g. lost 0.1549 g. at 92°. Calc. for the above formula: 10.75%. Found: 11.32%.

Preparation of the Compound $[(C_6H_5)_3COH]_4[CCl_4]_3$.—Triphenylcarbinol crystallizes from hot carbon tetrachloride on cooling in large, flat, square crystals. They begin to effloresce on being exposed to the air and soon become opaque. The compound was repeatedly prepared and analyzed on account of the fact that the analytical results did not agree with the simple formula that was anticipated from a consideration of the composition of the analogous compounds. The time during which the crystals were allowed to stand in the air was varied. The losses in weight in a series of analyses were as follows: 30.44, 30.87, 31.06 and 30.77%. The calculated loss for a compound containing one molecule of each constituent is 37.19% and for one containing two of the carbinol to one of carbon tetrachloride is 22.84%. The calculated loss for a compound of the formula given above is 30.75%.

Preparation of the Compound $[(C_6H_5)_3COH]_2(CH_3)_2CO$.—Triphenylcarbinol crystallizes from acetone in large, transparent, prismatic crystals which effloresce slowly.

0.6022 g. lost 0.0613 g. when heated to constant weight. Calc. for a compound of the above composition: 10.06%. Found: 10.18%.

Preparation of the Compound $(C_6H_5)_3CCl.CCl_4$.—Triphenylchloromethane crystallizes from carbon tetrachloride in small, lustrous crystals which do not effloresce rapidly in the air.

0.5073 g. lost 0.1444 g. at 92°. Calc. for the above formula: 28.92%. Found: 28.46%.

Preparation of the Compound $[(C_6H_5)_3CCl]_2.(CH_3)_2CO$.—A compound of this composition was obtained by allowing a solution of triphenylchloromethane in acetone to evaporate spontaneously. The addition product is relatively stable.

0.5916 g. lost 0.0553 g. at 92°. Calc. for the above formula: 9.43%. Found: 9.35%.

NASHVILLE, TENNESSEE.

[CONTRIBUTION FROM THE DEPARTMENT OF RESEARCH IN PURE CHEMISTRY, MELLON INSTITUTE, UNIVERSITY OF PITTSBURGH.]

ON THE DETECTION AND DETERMINATION OF HALOGENS IN ORGANIC COMPOUNDS.

BY I. DROGIN AND M. A. ROSANOFF.

Received January 13, 1916.

Some years ago C. W. Bacon,[1] at the instance of one of us (M. A. R.), undertook to test an apparently valuable method for determining halogens in organic compounds that had been recommended by Stepanoff in 1906.[2]

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[1] Bacon, THIS JOURNAL, **31**, 49 (1909).

[2] Stepanoff, *Ber.*, **39**, 4056 (1906).