# MOLECULAR REARRANGEMENTS.[1]

By William A. Noyes.

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"The end of chemistry *is its theory*. The guide in chemical research *is a theory*" (*Phil. Mag.* [4], **16,** 104 (1858)). With these words A. S. Couper began one of the most remarkable papers in the history of chemistry. At the time when he wrote the system of types advocated by Gerhardt had come into very general favor. Chemists were busy arranging the compounds of carbon and of other elements as well, in classes according to a few simple types, especially in accordance with the type of water and its multiples. The advantages of the system in comparison with what had gone before were very evident and organic chemistry was making rapid progress with its aid. It answered very well for the classification of many of the compounds then known and as a guide in the discovery of a great many new ones. And most of the chemists of that day, as always, were satisfied in working away at the discovery of a vast array of new facts and marshaling these in accordance with a highly mechanical theory with very little thought about its philosophical basis.

Under these conditions two master spirits, Couper and Kekulé, succeeded, entirely independently, in grasping those simple principles which lie at the foundation of our knowledge of the structure of compounds of carbon. Only as the result of an unfortunate accident was Kekulé's paper published before that of Couper.

It is interesting, and I think profitable, for us to recall that it was chiefly a consideration of the philosophical basis for Gerhardt's system which led Couper to reject it and propose something better. In criticizing the system he says of Gerhardt "He is led, not to explain bodies according to their composition and inherent properties, but to think it necessary to restrict chemical science to the arrangement of bodies according to their decomposition, and to deny the possibility of our comprehending their molecular constitution. Can such a view tend to the advancement of science? Would it not be only rational, in accepting this veto to renounce chemical research altogether?"

I have dwelt thus on Couper's point of view because it carries with it, as it seems to me, a lesson which we chemists of to-day may well take to heart. Very few are gifted with the insight of a Dalton, a Faraday, a Couper or a Rutherford but when a glimpse of the real things which lie beneath the phenomena which we observe comes to such an one it may guide the development of science for a decade, for a century, or even, if sufficiently true, for all time. And it seems possible that if we directed our thoughts more toward fundamental problems instead of towards the accumulation of compounds and of facts which are little more than permutations of compounds and facts already known, more real progress could be made.

The new principles proposed by Couper were very simple: First, that atoms show "degrees of affinity" or as we should call it, valence, and second, that carbon atoms can combine with each other. But these two simple principles have been the foundation on which chemists have built a knowledge of the structure of one hundred thousand compounds of

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[1] An address delivered at Worcester, Mass., September 14, 1909, at the celebration of the twentieth anniversary of Clark University.

carbon. These principles involve a knowledge of the actual arrangement of atoms within the molecule in the sense of the order of their successive attachments to each other. Thus far, at least, they are accepted by all active workers in organic chemistry and there is, among these, a practically universal belief that atoms and molecules actually exist and that there is something in the structure of the molecules which actually corresponds to our formulas. The two principles just stated have been further extended, especially by the study of optically active and of cyclic compounds to include still more definite ideas with regard to the actual arrangement of atoms in space and this development of stereochemistry has also received very general, though not quite universal, acceptance.

For a clearer understanding of molecular rearrangements we are in need of more definite knowledge with regard to the nature of those interatomic forces or attractions which hold atoms together in molecules and which also cause atoms of different molecules to react with each other. Many theories with regard to these forces have been proposed but none has, as yet, received any very general acceptance and the majority of chemists feel that any satisfactory knowledge of this sort is beyond our reach. But in 1858 nearly all chemists believed that any definite knowledge of the arrangement of atoms in chemical compounds was impossible, yet all of the facts for the acquirement of such knowledge were already in their hands and it only needed a clear statement of the simple principles proposed by Couper and by Kekulé and the application of those principles in the explanation of facts already known to make clear the structure of a large number of substances. Is it not possible that the answer to other, equally fundamental questions lies at our hands to-day?

It is in the hope that this may be so that I shall venture to state some of these fundamental questions as they present themselves to me.

The first of these is as to the nature of the attractive forces between atoms. The question is, perhaps, bound up with that of the nature of attraction between material bodies in general and may be equally far from a solution. Newton seems to have assumed an attractive force as an inherent property of matter and most of the discussion of atomic forces starts with a similar tacit assumption. But, as soon as the question is raised the mind revolts against the assumption of a force exerted through space without a medium. Physics has abandoned any idea of inherent attractive or repulsive forces in sound, light, heat or electricity and has accepted a kinetic explanation instead. Is it not probable that we must ultimately do the same for atomic forces? The discoveries in connection with radium have made us familiar with the notion that the atoms are very complex in their structure and that their parts may possess an almost inconceivable amount of kinetic energy. The spectroscope long ago demonstrated to us that such an atom as that of iron can send out impulses through the ether similar in complexity to those impulses of sound which come from a whole orchestra. It seems altogether probable that these impulses come from motions *within* the atom and not from vibrations of the atom as a whole. If we think of such intraatomic motions as general and that such motions within the atoms may produce effects which are transmitted through the ether, a kinetic explanation of atomic and molecular attraction seems possible.

The second question with regard to the atomic forces is whether these forces are purely attractive, resembling gravitation, or polar, partly attractive and partly repulsive, resembling or identical with electrical forces. You are all familiar with the fluctuation of opinion on this point. During the first half of the nineteenth century chemists came gradually to a pretty general agreement that the atomic forces are electrical in their nature. Then came the discovery of the substitution of chlorine for hydrogen in organic compounds and the overthrow of the old dualistic, electrochemical theory. Then for several decades the question of any connection between electrical and atomic forces was generally ignored and the attractions of the atoms were considered as direct and positive, though, of course, specific in character. During the last twenty years, as the theory of Arrhenius with regard to electrolytic dissociation or ionization has come into quite general favor, many different writers have proposed theories which identify atomic attractions with electrical forces. Faraday's law and the whole group of phenomena which find their most satisfactory explanation in the theory of ionization point very strongly toward an intimate relation between the two in the case of electrolytes. But if we assume that the forces which hold atoms together in electrolytes are electrical it is difficult to escape from the conclusion that the forces are electrical in the molecules of non-electrolytes also, for the two classes pass over into each other so gradually that it is very hard to believe that after the line is passed we are dealing with a radically different kind of atomic force. Further than this, an electrolyte may be formed in many cases by two different processes, by double decomposition in solution and by the direct union of the elements. Hydrochloric acid, acetylene and probably methane (from zinc methyl and by direct union of carbon and hydrogen) may be cited as illustrations. The nature of the compounds does not seem to depend at all on whether they are formed by the one process or by the other.

The idea that organic reactions are all ionic in character enables us, also to understand many reactions not so easily understood otherwise. Thus ethyl alcohol gives with phosphorus pentachloride, chlorethane, while phenol gives with the same reagent partly chlorobenzene, partly phenyl phosphate. If we assume, as seems natural, that ethyl alcohol ionizes to ethyl and hydroxyl while phenol ionizes partly in the same way but chiefly to hydrogen and phenoxy ions these reactions become clear:

$$4C_2H_5^+ + 3OH^- + O^{--} + H^+ + P^{+++++} + 5Cl^- = 4C_2H_5Cl + H_3PO_4 + HCl$$

or

$$4C_2H_5^+ + 4OH^- + PCl^{++++} + 4Cl^- = 4C_2H_5Cl + PCl(OH)_4$$

$$PCl(OH)_4 = H_3PO_4 + HCl$$

$$3C_6H_5O^- + 3H^+ + C_6H_5^+ + O^{--} + H^+ + P^{+++++} + 5Cl^- = C_6H_5Cl + (C_6H_5)_3PO_4 + 4HCl.$$

If we accept the reasons given and identify atomic and electrical forces we have still the question as to the real nature of these forces, for after we have called them electrical and even after we have identified them, perhaps, as residing in electrons (Faraday's law and many other things point that way) we still have the inherent difficulty of conceiving an attraction existing between bodies at a distance without a medium and I can not help a strong belief that we must ultimately have a theory for the attractions as an effect produced by the motions of the electrons.

Such a belief need not interfere with our use of the idea of positive and negative charges as a convenient present hypothesis. It may, perhaps, help us to a theory with regard to a reversal of the charge which it seems necessary to assume in certain cases and which has led to Abegg's theory of normal and contravalences. The hypothesis proposed by J. J. Thompson[1] that combination is caused by the transfer of negative corpuscles from one atom to another has much in its favor but it assumes inherent attractions between negative corpuscles and positive atoms or parts of atoms. Although the distances are small such attractions are in as much need of further explanation as is the force of gravity. We assume that the attractions and repulsions between conductors conveying currents or between magnets are due to motions in the ether between them. Is it not possible that the attractions and repulsions between corpuscles and atoms amy be explained in a similar manner?

The third and last question which I wish to raise is as to the nature of the forces which atoms already combined with other atoms exert in the attraction or repulsion of still other atoms. Are these residual forces merely the same forces which hold the atoms in combination still acting past those atoms which are nearest and upon others further away or are they different forces—as seems to be implied rather indefinitely in the "partial valences" of Thiele? The former idea seems simpler and more logical. This question is intimately associated with the mechanism of chemical reactions, the causes for the stability or instability of compounds and especially with questions of molecular rearrangements. As illustrations of facts requiring an explanation by a more intimate knowledge of forces of this sort we may cite the stability of the union of carbon with carbon in ethane as compared with oxalic acid, in propionic and butyric as compared with malonic and acetoacetic acids and in the esters of these acids as compared with the free acids, in benzoic acid as compared with 2,6-dimethyl-4-aminobenzoic acid (*Am. Chem. J.*, **20**, 813 (1898)) in hydrocinnamic as compared with phenyl propiolic acid and in acetic as compared with trichloracetic acid. The instability of compounds similar to those mentioned has long been accepted as an empirical fact and it is easy to predict many cases where such instability will occur but the reason for the instability has scarcely been discussed. With one exception the separation always occurs between two carbon atoms, one, at least, of which is united to a group or atom commonly designated as negative; and the exception may be only apparent, for the decomposition of 2,6-dimethyl-4-aminobenzoic acid takes place in an acid solution in which the amino group is combined with hydrochloric acid and may be considered negative.

It is very noticeable that acetoacetic acid, $CH_3COCH_2CO_2H$, is much less stable than pyrotartaric acid, $CH_3COCO_2H$. This is some slight indication that the separation of the carbon atoms is ionic in character, taking place more readily when there is a greater contrast between the atoms united together. It may be that, in this connection, we have

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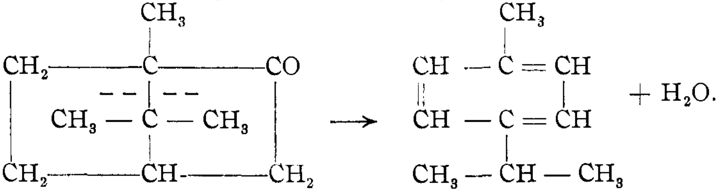
[1] "The Corpuscular Theory of Matter," p. 126. See also the recent discussion by Falk, *School of Mines Quarterly*, 30, 179 (1909). My own discussion of the reaction between chlorine and ammonia, THIS JOURNAL, **23**, 460 (1901), also has an important bearing on Thompson's hypothesis of the transfer of electrons in the union of atoms of the same element, *Loc. cit.*, p. 127.

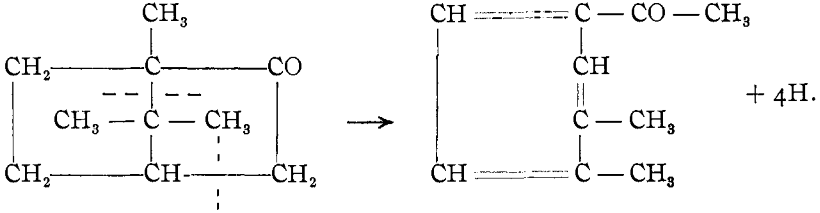
not sufficiently considered the difference between stability and reactivity. Thus sodium chloride and sodium nitrate are both instantaneously reactive in solutions, separating between the sodium and the chlorine or the sodium and the nitrate group but when heated the former compound is extremely stable while the latter decomposes between the nitrogen and oxygen rather than between the sodium and the nitrate group.

This leads me to the consideration of some of those molecular rearrangements in which I have been especially interested. When camphor is heated with phosphorus pentoxide it gives cymene.



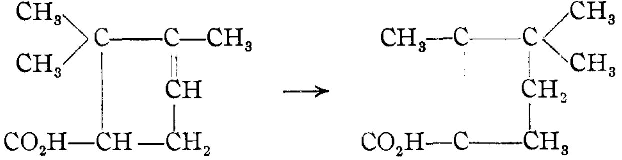
The two carbon atoms which separate from each other in this rearrangement bear the same relation to the carbonyl group as do the two carbon atoms which separate in either the acid or ketonic decomposition of acetoacetic ester. This primary separation of carbon from carbon is followed by the wandering of four hydrogen atoms, two of these leaving the molecule entirely with the oxygen.

When camphor is heated with sulphuric acid it undergoes a different rearrangement, giving *p*-acetyl-*o*-xylene (Armstrong and Kipping, *J. Chem. Soc.*, **63**, 81).



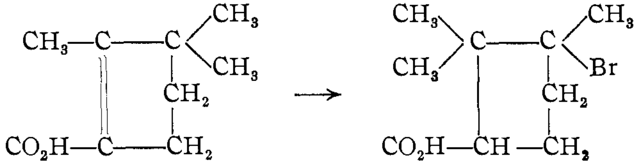
Here the rearrangement is much more complex and we must assume two primary separations of carbon atoms, both of which are again in the same relation as before to the carbonyl group. We have then a different carbon atom uniting with one of those which has separated, forming a six-ring and a transfer of a methyl group from one carbon atom to another, a transfer that has been noticed so many times in other compounds that it can no longer be considered abnormal. Four hydrogen atoms are lost but it is not necessary to consider that more than one hydrogen atom has wandered within the molecule.

When either dihydrohydroxycampholytic acid or α-campholytic acid is allowed to stand for a short time with dilute sulphuric acid (1 : 1) it is transformed into β-campholytic acid.



α-Campholytic acid. β-Campholytic acid.

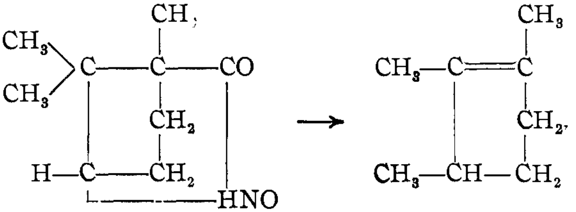
If β-campholytic acid is allowed to stand with concentrated hydrobromic acid it passes back to the hydrobromide of *dl*-α-campholytic acid:



β-Campholytic acid. *dl*-Hydrobromide of α-campholytic acid.

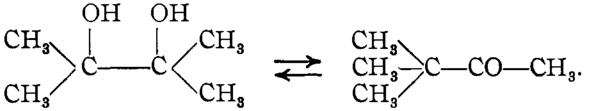
The latter compound may lose hydrobromic acid and give *dl*-α-campholytic acid, or it may exchange its bromine for hydroxyl giving *dl*-α-hydroxydihydrocampholytic acid (Walker and Cormack, *J. Chem. Soc.*, **77**, 380; Noyes and Blanchard, *Am. Chem. J.*, **36**, 285; Noyes and Patterson, *Ibid.*, **27**, 426).

In both of these transformations the methyl group separates from a carbon atom adjacent to a carbon atom which is doubly united to a third, just as in the acetoacetic ester the separation is from a carbon atom adjacent to one which is doubly united to oxygen. A similar relation, but with some variation is found in the transformation of the nitroso derivative of the anhydroaminolauronic acid to laurolene (Noyes and Derick, *J. Am. Soc.*, **31**, 669 (1909)).



Here the carbonyl group leaves (as carbon dioxide) a carbon atom attached to another which is united only to carbon. Doubtless the vibrations set up in the molecule at the moment of decomposition are an important factor in this rearrangement.

The pinacone-pinacolin rearrangement is, perhaps, the first of this type which was studied.



Tiffeneau and his collaborators have recently studied very many rearrangements similar to these, phenyl and other groups as well as methyl being transferred in many cases.

These shiftings of groups seem to take away from under us one of the most important principles on which we rely for the determination of structure, the principle that groups of atoms pass from one compound to another without changing their mutual relations. But when we think of the matter a little further we see that in all chemical reactions we expect the atoms to separate from each other at some point, and the only thing which surprises us is that a separation has taken place at a point where we did not expect it. We can already see some empirical relations between the compounds in which these separations and rearrangements take place and can predict to a certain extent where they are liable to occur. But we are still wholly in the dark as to the real forces which lie behind and are the cause of the transformations.

J. J. Thomson, Rutherford and others have shown that in the phenomena of conductivity of gases and of radioactivity we have new and most powerful means of studying the properties of matter and energy which have thrown a flood of light upon the nature of atoms. Ostwald at the other extreme has wished to discard atoms altogether and to explain structural organic chemistry on the basis of thermodynamics. Richards, from a somewhat intermediate point of view but with distinctly more sympathy with Ostwald than with Thomson, has given us a conception of compressible atoms which is surprisingly like the latter's corpuscular theory of chemical combination as developed in his latest book. Michael wishes to explain phenomena of this sort by the law of entropy. Thiele, imbued with the ideas of structure, explains them in part by partial valences. Still others have attempted to study such problems from the properties of crystals, the absorption of light, and a great variety of other phenomena. The great number of properties which must finally be coördinated in any true explanation of atomic and molecular forces is discouraging and gives some basis for that agnostic point of view which considers the number of possibilities infinite and that we can never hope for a knowledge of the truth even as to the existence of atoms. Let us rather take the more hopeful view that some one, in a not too distant future, will give us a simple and comprehensive theory of the nature of atoms and of the forces which bind them together in compounds. The one who is to do this must not look at science as cut up into water-tight compartments but must be able to coördinate the evidence which comes from workers in many diverse fields of chemistry, of physics and of other sciences.

URBANA, ILL.

## NEW BOOKS.

**Elements of Chemistry.** By HOLLIS GODFREY. Girls High School, Boston, Mass. 448 pp. New York: Longmans, Green and Co Price, $1.10.

This book is written in an entirely different style from most text books on chemistry; interest is made the prime object and exactness in details is often sacrificed to this end. Its object is to cover the whole field, not requiring any laboratory work or lecture experiments to accompany it. In taking up the discussion of a substance the practical application is first made apparent and then the general properties and mode of preparation are considered. The manner of presenting the subject should attract younger students and stimulate their interest to a wider knowledge of the subject. The book is profusely illustrated, almost to excess, as some of the illustrations are not well chosen. A very complete review-chapter and a chapter of questions follow the main text.

The book would be of no use in a college but is particularly well adapted