

Chemistry. — “*The Condition of Motion of the Molecules in Space.*” By Prof. J. BÖESEKEN. (In collaboration with MESSRS. CHR. VAN LOON, DERX, and HERMANS).

(Communicated at the meeting of October 29, 1921).

In a paper on the configuration of the tartaric acids (BÖESEKEN and Coors)¹⁾ the conclusion was drawn from the behaviour of these acids and their esters towards boric acid, that the carboxyl groups, both when substituted and when not substituted, were as far apart as possible.

The amides and ethyl-amides, however, presented deviations, so that this simple assumption did not suffice. The great influence which these substances have on the conductivity of boric acid, points to a favourable situation of the hydroxyl groups with regard to each other, which can only satisfactorily be accounted for, when there are *attractive* actions between these groups and the substituted or non-substituted amide groups.

Further for a comparatively large number of α -glycols no influence on the conductivity of the boric acid was found; these OH-groups must, therefore, lie far apart, which could again be explained by mutual repulsion. At any rate it appeared from these investigations that atoms that are not directly bound to each other, also exert an action on each other, and we may expect that the state of equilibrium of a molecule will be the result of all the forces in that molecule, both the attractive and the repulsive ones.

I have already pointed out²⁾ that every change in the position of the atoms, however slight, must give rise to re-arrangements, through which the position of *all* the parts of the molecule will not remain exactly the same.

In the molecule-halves of active and inactive tartaric acid e.g. the comparable groups will no longer be perfectly identical; hence the principle of the optical superposition cannot be valid.

In consequence of the action of these forces, molecules which up to now have been considered as symmetrical, as the anti-tartaric

¹⁾ Versl. Kon. Ak. Wet. **29**, 368 (1920). Has not yet appeared in English.

²⁾ " " " " **29**, 562 (1920). " " " " " " "

acid, will no longer have mirror images that cover each other, which can easily be demonstrated by means of the well-known carbon models.

Only two positions of the anti tartaric acid are symmetrical, viz. that in which the equal groups lie on the same side of the axis of the central C-atoms as close as possible to each other and that in which they lie on both sides as far from each other as possible. It would be quite accidental, that one of these positions should be the most stable state of equilibrium under all circumstances.

This seems in conflict with experience. We should, however, bear in mind the following considerations. In view of the limited number of isomers it has already long been assumed that the molecule halves can move round the single bonds as axes in opposite direction or with different velocities.

When we supplement this necessary condition with the hypothesis that these movements also continually take place in this sense that the most stable position of all the positions possible at the moment will occur most frequently, and that, therefore, the molecule executes irregular rotations or oscillations round this position, there is no longer any contradiction with experience.

When we consider these rotations round the bond of the central carbon atoms of the anti-tartaric acid, we see that in one full rotation of one part with regard to the other, the molecule will twice pass a symmetric position.

At these moments the molecule is optically inactive, and since now the chance has become equally great that the stable asymmetric-position will be reached by a movement in the direction of the hands of a clock or in opposite direction, a continual racemisation will take place.

Though the state of equilibrium is asymmetric, we shall probably never observe the optical activity in liquid or dissolved state.

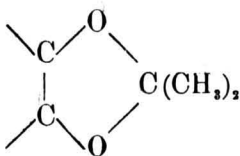
This dynamic representation, which is forced upon us by the inactivity of the anti-tartaric acid, applies, of course, to all saturated molecules. Our observations of the behaviour of the α glycols towards boric acid and acetone can be explained most simply in this way.

The saturated non-cyclic α -glycols do not increase the conductivity of the boric acid; we have drawn the conclusion from this that the hydroxyl-groups are not favourably situated, and have accounted for this by the assumption that the OH-groups repel each other, through which they can get as far as possible from each other owing to the mobility of the molecule.

According to the dynamic representation this position will be the

most stable state of the molecule, but all the other positions will also be realized, albeit less frequently, and the more rarely as the state deviates more considerably from the most stable.

Of the α -glycols there are cyclic acetone-compounds known, which are formed with excess of acetone, to which a little HCl or H₂SO₄ has been added, and which are stable, when there is not a trace of these last catalysts present.



There is every reason to assume that there is the greatest chance that these compounds are formed when the OH-groups are situated in the plane with the C-atoms to which they are bound, and on the same side of them. When the OH-groups repel each other, this will seldom take place, but by taking a very great excess of acetone, we shall yet be able to obtain a pretty large quantity of the cyclic compound, which can be retained by removal of the catalyst, and which can be freed from the acetone by fractional distillation.

When the OH-groups cannot get into the most favourable position, or near it, as in some cyclic trans 1.2-diols, where the free rotation through the ring is prevented, no acetone-compounds will be formed. This now has been found, and this renders a firm support to this dynamic representation (see below).

The saturated glycols can, however, always assume the most favourable position, though it be only rarely; the relative frequency of this case may be judged from the state of the equilibrium:



By determination of the constant of equilibrium:

$$K_t = \frac{C_{\text{glycol}} \times C_{\text{acetone}}}{C_{\text{comp.}} \times C_{\text{H}_2\text{O}}}$$

a measure is supplied for this frequency, and so also a measure for the situation of the hydroxyl groups in the most stable position of the molecule.

Here follows a summary of the constants of equilibrium of some glycols: ¹⁾

¹⁾ In his thesis for the doctorate (Delft 1919, p. 59) "over de Stereochemie der cyclopentaandiolen 1.2 en hydrindeendiolen 1.2". Mr. CHR. VAN LOON was the first to point out that the study of these equilibria would probably bring to light minuter differences in the configuration of the molecules than the boric acid method. The measurements were carried out by Mr. P. HERMANS.

	K_{18°
ethylene glycol	0.14
propane diol 1.2	0.44
" 1.3	0.026
α -monochlorhydrine	0.28
glycerine	0.77
cis-cyclohexanediol 1.2	0.15
trans- " 1.2	0.000

The study of the cyclic glycols has supplied an important support to the efficiency of the dynamic representation.

In the cyclo-pentane-diols the five carbon atoms lie in one plane almost without tension when we assume that the directions of affinity make an angle of $109^\circ 28'$ with each other. In the cis-isomers the OH-groups lie almost in one plane with the C-atoms, to which they are bound, hence very favourably for boric acid and acetone, as has appeared from VAN LOON's investigation.

In the trans-diols the position is very unfavourable. In consequence of the five-ring the position of these OH-groups can never become favourable without the ring being broken. Indeed there was no question of the formation of an acetone compound.

The absence of the acetone-compound in this trans-diol and in the trans-hydrindene diol 1.2 is also the proof that when the OH-groups are prevented from getting from time to time into or almost into one plane, no five-ring is formed. (see above).

At the time it was found that cis-cyclohexane diol 1.2 has no influence on the conductivity of the boric acid. This had led me to conclude already then that this six-ring must be assumed to have a certain suppleness, through which the hydroxyl groups would get somewhat further from each other than would have been expected, if the six atoms of the ring lay permanently in a plane.

The equilibrium: glycol + acetone \rightleftharpoons acetone compound + water corroborated on one side this view, as its position is almost as unfavourable as with the ethylene glycol (see above).

On the other hand it corroborated our dynamic view: The acetone compound is formed; hence the hydroxyl groups must now and then lie in or almost in the same plane as the adjacent C-atoms.

A complete rotation, as is the case with the saturated non-cyclic glycols, is not possible here, as this would mean a continual transition from cis- into trans-diol, and vice-versa, which does not take place; besides, the trans-diol gives no trace of an acetone compound.

How can we now form an idea of the movement in the cyclohexane diol?

In 1890 an extensive study was published by SACHSE¹⁾ on the position of the C-atoms in the saturated ring systems starting from the premise that the directions of affinity form angles of $109^{\circ}28'$ with each other. He proves for the three-, four-, and five-rings that the atoms must be situated in one plane, and that a tension is inevitable, which is, however, insignificant for the five-ring. (VON BAYER'S ring tension). He shows for the six-ring that the molecule can escape a tension in two ways. First of all the C-atoms can lie three in one plane, and three in another, so that the bonds between the C-atoms form a zig-zag line. It is, however, also possible that four atoms lie in one plane, and two (e.g. 1 and 4, 2 and 5 or 3 and 6) outside it.

To bring the molecule out of the first position, a certain resistance must be surmounted; the second position is pliable.

It has been pointed out on different sides that these positions of the molecule could not form the image of the stable situation of the atoms, because the number of isomers, and particularly of optical isomers would then have to be much greater.

ASCHAN²⁾, however, remarks, that these positions *are* possible when they are considered as the successive phases of a system in motion.

This view, indeed, has been confirmed by our boric acid measurements and the study of the acetone-compounds.

When we accept the view that the molecules of the six-rings move through space as undulatory surfaces, the OH-groups of the cis-diol get from time to time into the same plane with and on the same side of the C-atoms to which they are attached, and the frequency of this occurrence will depend on the most stable state of the molecule.

It is clear that in these undulations repeatedly a symmetric position is passed, so that, though the most stable situation is an asymmetric one, the separation of optical isomers in liquid state is not very well possible; for racemisation will continually set in for

¹⁾ Berichte **23**, 1363 (1890). Zeitschr. f. physik. Chemie **10**, 228 (1890).

²⁾ "Chemie der Alicyclischen Verbindungen", pag. 328—331.

the same reason as with the movements of the anti-tartaric acid. In the trans-cyclohexane diol the OH-groups always remain very far apart; indeed, we have not been able to obtain an acetone-compound, nor has an influence been observed on the conductivity of the boric acid.

Another confirmation was furnished by the cis- and trans-cycloheptane diols.

When SACHSE's calculations are applied to them, the OH-groups, both in the cis- and in the trans-diol, get in their movements into, or nearly into the same plane with and on the same side of the C-atoms, which they adjoin. Now acetone compounds have actually been obtained, and increase of the conductivity of boric acid has been observed, *both in the cis- and in the trans-diol*; accordingly our measurements are in perfect harmony with what is to be expected in the movements of this system as undulatory surface.

According to this view there is, therefore, no tension in the six- and sevenring-systems, even less than in the five-ring, and in fact, we knew this already from the measurements of the heats of combustion of the cyclo-paraffins. The very accurate determinations by STOHMANN, ROTH, and ZUBOW leave no room for doubt that the increase of the heat of combustion per CH_2 -group of C_5H_{10} , C_6H_{12} , C_7H_{14} does not amount to more than has been found in the paraffins, which ought to have been the case with increasing tension.

This result seems to be in conflict with the experiences obtained about the ring-closures. When there is no ring-tension present in the saturated rings with more than six atoms, why are not they formed as easily as the five-rings, and why are they also clearly less widely spread in nature?

This more difficult formation is, indeed, strikingly illustrated by the very low constant of equilibrium of the system propane diol 1.3 + acetone, especially when compared with the corresponding propane diol 1.2 + acetone, the difference of which rests on six-ring closure against five-ring closure (see above).

An answer is easy to give also here.

The probability that the two OH-groups in the propylene glycol 1.2 assume a favourable position with regard to the acetone molecule is so much greater than for the 1.3 isomer. In the propane diol 1.2 a rotation of the molecule parts round a single bond suffices, whereas in the propane diol 1.3 the paths of the OH-groups are much more involved and intricate, so that in the same space of time they will certainly assume a favourable position much less frequently.

We may summarise the result of this study as follows:

1. Also atoms that are not directly bound to each other, exercise an action on each other in the same molecule.

2. The saturated non-cyclic molecules execute, among others, movements in which the parts of the molecule revolve in opposite direction or with different velocities round the single bonds as axes.

In case of not uniform load, as is the case in by far the most molecules (excepted are only H_2 , O_2 , N_2 , etc. C_2H_6 , C_2Cl_6 , perhaps oxalic acid, etc.) the movements are irregular, because the most stable position of the atoms will be passed most frequently.

3. In the saturated ring-shaped molecules with six and seven carbon atoms the ring-forming atoms are not fixed in one plane, but they lie tension-less in a curved surface, which travels through space in undulatory movements.

Delft, October 1921.
