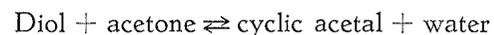


Chemistry. — *On the sterical conditions in the cyclic acetone-acetals of the ortho-di-phenols.* By J. BÖESEKEN.

(Communicated at the meeting of February 25, 1939.)

After CHR. VAN LOON¹⁾ had pointed out the significance of the formation of cyclic acetals of polyols for the knowledge of the position in space of the hydroxyl groups, HERMANS²⁾ studied very elaborately the equilibria

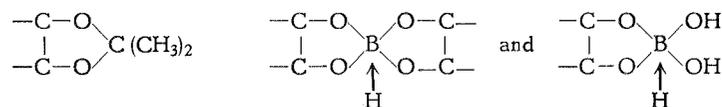


in a number of typical cases.

It was a well-known fact that the increased conductivity of boracic acid produced by polyols is closely connected with the position of these groups in space.

HERMANS now observed that upon the whole the acetone equilibria were situated more to the right according as the influence of the boracic acid increased.

From the boracic acid researches³⁾, lastly those of VERMAAS⁴⁾, it became apparent that the increased conductivity is due to the presence of complex mono-diol and didiol boracic acids, the structure of which was long since known, owing to their isolation, analysis and characteristics²⁾. These are also cyclic acetals, with this difference that the boron atom takes the place of the carbon atom.



The boron atom is coordinatively tetravalent, which implies that the boro-complexes are strong acids, in contrast with the ordinary cyclic acetals which naturally are neutral.

If the sterical conditions, viz. the distances between the atoms, in the boracic acid compounds may be compared with those of the cyclic acetals, it was to be expected that the increase in conductivity and the position of the acetone equilibrium run parallel and consequently the researches by

¹⁾ CHR. V. LOON, Stereochemie der cyclopentaan- en der hydrendeen diolen-1-2. Diss. Delft 1919.

²⁾ P. H. HERMANS, Onderzoek naar de ruimtelijke configuratie van enkele glykolen. Diss. Delft 1924.

³⁾ J. BÖESEKEN, Configuration des polyalcools. Conférence devant la Soc. Chim. de France. 16 juin 1933.

⁴⁾ N. VERMAAS, Rec. trav. Chim., **51**, 67 et 955 (1932).

J. BÖESEKEN and N. VERMAAS, Journ. of Phys. Chem., **35**, 1477 (1931).

HERMANS may be considered as an indication that these distances are indeed of the same order of magnitude.

It was surprising, therefore, that the ortho-di-phenols, which produce a considerable increase in the conductivity of boracic acid and also yielded the first well crystallized boro-complexes, seemed to yield no cyclic acetone compounds.

From an investigation by G. SLOOFF⁵⁾ it now appeared that these compounds indeed can be prepared, if the formed water is removed by means of powerful dehydrators, such as P₂O₅ and fuming H₂SO₄.

The possibility of formation was thus demonstrated but from the manner of this formation it is yet clear that the acetone equilibria have a very unfavourable position, which has been confirmed by G. SLOOFF.

In order to obtain this equilibrium, a small quantity of a powerful catalyzer must be sufficient. If in some way or other the formed water is regularly removed, it is to be expected that the acetal may be obtained in satisfactory yields. This removal of the water may take place by a physical method, viz. by boiling the equilibrial mixture with a neutral liquid, e.g. an aromatic hydrocarbon. The vapour takes the water vapour with it. Subsequently, by condensation of this mixture, the heavier water may be separated from the lighter hydrocarbon and the latter led back into the reaction retort.

This method has been successfully carried out by V. D. SPEK⁶⁾ for a great number of aromatic ketone acetals. Particularly for ketones with a fairly high boiling-point it appeared to be very effectual. For acetone itself this method is not suitable, since this is too volatile and consequently is removed with the hydrocarbon. Water is easily dissolved in acetone; consequently no separation of the layers sets in.

From the amount of water caught it may be found how far the reaction has proceeded. The longer duration of the condensations again shows that the acetal equilibria are very unfavourably situated.

SLOOFF (l.c.) has tried to explain this unexpectedly unfavourable position of the hydroxyl groups with regard to the ketone-condensation. He pointed out that the distance between the boron and oxygen atoms may be considerably larger than between C and O, so that the oxygen atoms of the diphenols can be more easily attacked by the boron atom than by the carbon.

V. D. SPEK on the other hand is inclined to think in the first place of the nature of the phenolic hydroxyl group, since, as appears from the behaviour of aldehydes and ketones towards the phenols, only rarely normal acetal formation sets in, but other condensations, e.g. the formation of diphenyl methane derivatives take place.

⁵⁾ G. SLOOFF, Cyclische aethers, gevormd door condensatie van pyrocatechol met aldehyden en ketonen. Diss. Delft 1934. See also Rec. trav. Chim. **54**, 995 (1935).

⁶⁾ J. J. V. D. SPEK, Cyclische acetalen van pyrocatechol. Diss. Delft 1938.

His opinion is supported by the behaviour of naphthalene diol 1.8, which produces an exceedingly strong increase in conductivity and where indeed the hydroxyl groups for the acetal formation (according to the calculations by SLOOFF) would have a more favourable position than those of pyrocatechol, and yet no cyclic acetal can be obtained with acetone. (It may be done with other ketones, though with a bad yield.)

I do not consider this argument of great value, since this diphenol in the presence of powerful catalyzers very easily resinifies and the mobility of the aromatic H-atoms is so great that other condensations than the acetal formation very easily set in.

Since, for the rest, the whole investigation of V. D. SPEK is based upon the equilibrium reaction of the cyclic acetals and the elegant method applied by him often yields excellent results, I am inclined to think that the explanation given by SLOOFF is the correct one. Here we have to consider also that the phenolic hydroxyl groups are kept in their places by the tension in the benzene ring, whereas aliphatic hydroxyl groups by the suppleness of the saturated bonds and, by the unimpeded rotation round the single bond, may far more easily be brought into a position which is more favourable to the acetal formation.

It is, therefore, not only the unfavourable position of the hydroxyl group but also the fact that they are, so to speak, fixed in this position, which drives the acetal equilibrium so far to the left.

Taking into consideration the most probable distances between the atoms, C—C(ar) 1.39; C—O 1.36; B—O 1.53; and assuming that the phenolic hydroxyl groups form angles of 120° with the benzene nucleus, we find a distance between the two O-atoms of 2.75 Å, not sufficient to be attacked by the C-atom, the double C—O distance being 2.72 Å, the double B—O distance 3.06, so quite sufficient.

For the formation of cyclic acetal an inward bend of the phenolic oxygen atoms is necessary and with these stiff groups this requires special energy. In connection with this slight suppleness of the groups linked to the nucleus, it may be expected that in the cyclic acetals the tension will remain.

In order to examine this, Miss DE QUANT determined the heat of combustion⁷⁾ of an aromatic and some aliphatic cyclic acetone acetals and of the polyols themselves⁸⁾, from which it became indeed apparent that the difference in heat of combustion of acetal and polyol in the aromatic compound exceeded by far the corresponding differences of the aliphatic compounds. The small differences in the highly divergent aliphatic diols are interesting and evidently indicate that in the supple

⁷⁾ This was done in the laboratory and under the guidance of Prof. Dr. Ir. P. E. VERKADE at the Nederlandsche Handelshoogeschool at Rotterdam, whom I wish to thank also in this place for his hospitality and assistance.

⁸⁾ J. H. DE QUANT, De verbrandingswarmte van eenige diolen en hun aceton-verbindingen. Diss. Delft 1938.

Acetone acetal of	Δ per acetal group
mannitol (tri)	423.5
„ (di)	423.9
„ (mono)	422.2
hydrobenzoine	422.8
cis . hydrendene diol 1.2	420.9
cis . tetrahydronaphtalene diol 2.3	419.4
cis . phenyl-1-cyclopentane diol 1.2	415.0
protocatechuic acid	440.2

acetal hardly any tensions are present, even in a case where we know with certainty that in the diol the hydroxyl groups have an unfavourable position (hydrobenzoine).

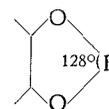
The significance of a slight heat of combustion, as in the case of cis . phenyl-1-cyclopentane diol 1.2, cannot be explained without a much larger experimental material.

Although it has to be admitted that the phenolic hydroxyl groups differ also chemically from the alcoholic ones, yet it must be concluded from these researches that the different behaviour of these groups towards boracic acid and acetone is mainly based on sterical grounds. The difference in distance of the coordinatively tetravalent boron atom and the tetravalent carbon atom to oxygen on the one hand and the stiffness of the phenolic hydroxyl group in contrast with the suppleness of the alcoholic group on the other hand offer a satisfactory explanation.

Finally I may draw attention to the fact that the influence of the poly-

Polyphenol	Δ mol
pyrocatechol	1012
pyrogallol	1140
hydroxy hydrochinol	644
dinitropyrocatechol	± 31000
dihydroxynaphtalene 1.2	2080
„ 2.3	3400
„ 1.8	134000
protocatechuic acid	2200
gallic acid	900

phenols upon the conductivity of boracic acid is not extraordinarily great and only shows considerable differences, as may be seen in the table, if special causes can be expected. Assuming that the angles between the bonds of the nucleus and of the substituent are 120°, we may calculate from the known distances between the atoms that the angle between the boron atom and its affinity directions is about 128°: In connection with the slight suppleness of the aromatic bonds, this is indeed hardly favourable. For 1.8 dihydroxy



naphtalene we calculate 104° , which is far more favourable and is reflected in the uncommonly high value for the increase in conductivity. Considering the problem in this light, we must assume that the nitro groups in dinitropyrocatechol bend the hydroxyl groups towards each other. A slight decrease of the two angles of 120° has immediately a strong influence upon the angles of the central boron atom.

Delft, February 1939.

Mathematics. — *Die projektiven Invarianten von vier und fünf Geraden im R_4 .* Von R. WEITZENBÖCK.

(Communicated at the meeting of February 25, 1939.)

Bei Geraden $a, a, p, m, \varphi, \dots$ im vierdimensionalen Raume R_4 ergeben sich auf geometrischem Wege wie folgt die einfachsten projektiven Invarianten: wir verbinden die Geraden a und a zu einem linearen $R_3 S'_{12}$, ebenso p und m zu einem Raum S'_{34} . Diese beiden Verbindungsräume schneiden sich in einer Ebene ($S'_{12} S'_{34}$). Sie trifft die fünfte Gerade φ , wenn die Invariante

$$\sum_{ik} \varphi_{ik} (S'_{12} S'_{34})_{ik} = A_{5,12,34}$$

verschwindet.

Ich beweise im Folgenden, dass sich bei vier und bei fünf Geraden im R_4 jede projektive Invariante durch Invarianten $A_{i,jk,rs}$ der genannten Art ausdrücken lässt. Ueberdies bilden diese Invarianten bei willkürlich vielen Geraden auch eine Rationalbasis für alle projektiven Invarianten.

§ 1. Allgemeines.

Wir gehen aus von einer Anzahl willkürlicher Geraden des vierdimensionalen Raumes in allgemeiner Lage mit den Koordinaten

$$a_{ik}, \alpha_{ik}, p_{ik}, m_{ik}, \varphi_{ik}, \dots \dots \dots (1)$$

und stellen diese Koordinaten dar mit zweifältigen Komplexsymbolen

$$a_{ik} = a_i a_k = b_i b_k = c_i c_k = \dots$$

wobei also b, c, \dots mit a äquivalent ist. Ebenso seien β, γ, \dots mit α ; q, r, \dots mit p u. s. w. äquivalent.

Nach dem ersten Hauptsatz der symbolischen Methode ist dann jede ganze rationale projektive Invariante der Geraden (1) ein Produkt von Klammerfaktoren der Gestalt $f = (a \alpha p \pi \varrho)$, über die man eine Reihe von Voraussetzungen machen kann u. zw.:

a. Jedes f hat die Gestalt $(apma^2)$, enthält also mindestens zwei gleiche Reihen. In

$$J = (a \alpha p \pi \varrho) (a \dots) \dots$$

lässt sich nämlich die Reihe a des zweiten Faktors in den ersten hineinbringen¹⁾.

¹ Vgl. meine "Invariantentheorie", Groningen, p. 79, (1923).