A rotation diagram with a face diagram as axis (110) gave a zone distance $\sqrt{2}$ times as large as that of a (100) diagram.

This is an indication of a face-centred-translation-lattice. Also the extinctions in the DEBIJE—SCHERRER diagram are in agreement with this. We have therefore a face-centred-cube lattice. A calculation of the intensities shows that only the space-group O^4 is possible with the following point-arrangement.

$$Au \begin{cases} \tfrac{1}{8}\ \tfrac{1}{8}\ \tfrac{1}{8}, & \tfrac{5}{8}\ \tfrac{5}{8}\ \tfrac{1}{8}, & \tfrac{5}{8}\ \tfrac{1}{8}\ \tfrac{5}{8}, & \tfrac{1}{8}\ \tfrac{5}{8}\ \tfrac{5}{8}, & \tfrac{1}{8}\ \tfrac{7}{8}\ \tfrac{7}{8}, & \tfrac{5}{8}\ \tfrac{3}{8}\ \tfrac{7}{8}, \\ \tfrac{5}{8}\ \tfrac{7}{8}\ \tfrac{3}{8}, & \tfrac{1}{8}\ \tfrac{3}{8}\ \tfrac{3}{8}, & \tfrac{7}{8}\ \tfrac{1}{8}\ \tfrac{7}{8}, & \tfrac{3}{8}\ \tfrac{5}{8}\ \tfrac{7}{8}, & \tfrac{3}{8}\ \tfrac{1}{8}\ \tfrac{3}{8}, & \tfrac{7}{8}\ \tfrac{5}{8}\ \tfrac{3}{8} \\ \tfrac{7}{8}\ \tfrac{7}{8}\ \tfrac{1}{8}, & \tfrac{3}{8}\ \tfrac{3}{8}\ \tfrac{3}{8}, & \tfrac{3}{8}\ \tfrac{7}{8}\ \tfrac{5}{8}, & \tfrac{7}{8}\ \tfrac{3}{8}\ \tfrac{5}{8} \end{cases}$$

$$Bi \begin{cases} \tfrac{1}{2}\ 0\ 0, & \tfrac{1}{2}\ \tfrac{1}{2}\ \tfrac{1}{2}, & 0\ 0\ \tfrac{1}{2}, & 0\ \tfrac{1}{2}\ 0, \\ \tfrac{3}{4}\ \tfrac{1}{4}\ \tfrac{1}{4}, & \tfrac{3}{4}\ \tfrac{3}{4}\ \tfrac{3}{4}, & \tfrac{1}{4}\ \tfrac{1}{4}\ \tfrac{3}{4}, & \tfrac{1}{4}\ \tfrac{3}{4}\ \tfrac{1}{4} \end{cases}$$

The second possible point-arrangement is the above one displaced over half an identity period. Thus the gold and bismuth atoms are situated at points non-equivalent for the structure and therefore not statistically distributed, so that we can speak of Au_2Bi combination in which neither gold nor bismuth is soluble. We have, therefore, to do with a singular kind of crystal, which is in good agreement with the very low magnetic threshold value [1]) of the gold-bismuth. This is of the same order of magnitude as that of the pure supraconductors [2]). Until now always high magnetic threshold values have been given for solid solutions.

The results of the measurements and a complete discussion of the structure will appear in the next communication.

[1]) Comm. Leiden No. 214b. These Proc. XXXIV, p. 56.
[2]) Comm. Leiden No. 191b. These Proc. XXXI, p. 687.

Chemistry. — *Oxidation of phenol with peracetic acid. (Contribution to the knowledge of the substitution of benzene).* By Prof. J. BÖESEKEN.

(Communicated at the meeting of June 25, 1932).

Some years ago G. SLOOFF and one of us (B.) discovered that at the oxidation of naphtalene with peracetic acid a very considerable quantity of o-carboxy-cis-cinnamic acid is produced. So one of the benzene-rings of the naphtalene is opened, by which probably the naphtalene o-chinone as intermediate product is formed, because this is quantitatively oxidized by peracetic acid to o-carboxy-cis-cinnamic acid. (By the way we remark that this does not prove that in naphtalene there are one ring of benzene and one unsaturated ringsystem). They found that benzene was not attacked by 10 % peracetic acid, which statement we can confirm.

By introducing a hydroxyl-group in benzene, the ring becomes much more sensitive towards peracetic acid.

Some preliminary experiments with 10, 20, and 75 % peracetic acid showed that with more diluted solutions the oxidation proceeded regularly :

when oxidized with 75 % peracetic acid, the solution had to be cooled; next to relatively little cis-cis-muconic acid, fumaric acid was formed.

As by these preliminary experiments in all cases muconic acid m. p. 187° was obtained — to which because of its formation out of ortho-chinone we gave the cis-cis configuration [1]) — and as this requires for its formation out of phenol three molecules of peracetic acid, we added this amount.

As to these preliminary experiments the following details may be given:

For instance 10 gr. phenol were dissolved in 74.2 gr. 20 % peracetic acid; after 10 days the titre of the peracetic acid remained constant.

At first there is no colouring; after that a more and more intense red colour appears; after five days a white precipitate is formed, which after 10 days does not increase any more.

This white precipitate is filtered and has been recrystallized twice.

M. P. = 187°

$$\left. \begin{array}{l} 0.1424 \text{ g} \quad 9.3 \text{ cc } 0.218 \text{ n KOH} \\ 0.2821 \text{ g} \quad 18.10 \text{ ,,} \quad \text{,, ,, ,,} \end{array} \right\} \text{aeq. weight} = 71 \text{ (Mol. weight} = 142)$$

Elementar analyses; found 50.0 % C and 3.9 % H,

Calc for $C_6H_6O_4$ = 50.7 % C and 4.2 % H, aeq. weight 71 (mol. weight 142).

The filtrate is distilled in vacuo; after the distillation of the main quantity of the acid, long red needles begin to crystallize in the distilling flask. If we wash out the flask with ether, which is then vaporised, a syrup remains in which we find red needles and a colourless substance; these are put on a porous plate; the solid substance is extracted again with ether; a little muconic acid remains; after evaporation of the ether the red needles are this time left behind in pure condition. This appeared to be pheno-chinone m.p. 71°.

The syrup, which had penetrated into the porous plate was gathered in the following experiment; it had great reducing power and gave a precipitate with 2.4-di-nitro phenylhydrazine, which indicates the formation of a substance with aldehydic properties.

At the oxidation of 5 gr. phenol with 50 gr. 70.5 % peracetic acid the following phenomena were observed: the solution reddens at once, evolving large quantities of heat, which necessitates cooling. After some days the colour begins to diminish and is at last pale yellow, while a white precipitate is formed. This precipitate is cis-cis-muconic acid; the filtrate is vaporized at a pressure of 20 mm.; a pale yellow substance remains, which is soluble in water, has an acid reaction, discolours $KMnO_4$, gives the silver-mirror reaction and with 2.4 dinitrophenylhydrazine produces a little of a red precipitate.

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[1]) This has in the meantime been confirmed by oxidising the acid with $KMnO_4$ which produces besides oxalic acid exclusively anti-tartaric acid (see next proceedings).

The melting point 194° is wrong, this ought to be 187°—188°.

When recrystallized out of aethylacetate it appears to be principally a white crystallized substance, m.p. 284°, acid, aeq. weight 61 ; on heating water is evolved besides a sublimate m.p. 51° ; i.e. *fumaric acid.*

Evidently the pheno-chinone is oxidized further by the very strong oxidizing agent and at last fumaric acid is formed.

During the final experiment 10 gr. phenol were oxidised with 210 gr. 10 % peracetic acid until the precipitate of muconic acid did not increase any more : the amount of this acid was 4.3 gr. An iodometric titration of the peracetic acid gives no good results, because pheno-chinone also liberates iodine from *KI.*

The filtrate is vaporized in vacuo, while the distillate, after decomposing the per acid by finely powdered platinum, is titrated with *KI* to determine the pheno-chinone.

Total of distillate : 212 gr. :   15.86 gr. requires   8.1 cc. 0.097 n thio

31. 75 gr. requires   16.15 cc. n thio

Average 0.233 gr. phenochinone

Altogether formed **1.6 gr.** phenochinone.

The rest of the distillate was extracted with a little dry ether : 1.1 gr. muconic acid remains. Altogether there was formed 5.4 gr. cis-cis muconic acid. The etheric solution gives, after distillation of the ether, a dark red syrup : this contains besides substances with reducing power chiefly pheno-chinone. As this cannot be titrated iodometrically, the whole was reduced with SO_2 ; then a small part of it is oxidized with $FeCl_3$, after that extracted with low-boiling petrol-ether ; after this the pheno-chinone crystallized in long red needles. When titrated iodometrically this amount distributed on the total quantity of residue comes to 3.1 gr.

Total amount 1.6 + 3.1 = **4.7 gr. phenochinone.**

So 10 gr. phenol have produced

5.4 gr. muconic acid aeq. to 3.6 phenol

4.7 gr. pheno-chinone aeq. to 4.4 phenol.

Consequently 80 % of the phenol is recovered. We tried to isolate other products from a part of the reduced liquid, which thus contains hydrochinol and phenol, after eliminating the excess of SO_2 by boiling the liquid. This was therefore treated with bromine ; only some tribromophenol (m.p. 92°) and distributed on the whole quantity, 6.5 gr. (equiv. to 2.92 gr. phenol) and a little monobromohydrochinol could be isolated.

From the results of this experiment of oxidation the following conclusion can be drawn : As in 4.7 gr. phenochinone 3.1 gr. of phenol are bound, 10.3—3.1 gr. = 6.9 gr. phenol are oxidized, of which 3.6 gr. in the direction of muconic acid and 4.7—1.3 = 1.6 gr. in the direction of p-chinone. Of 1.7 gr. of phenol the destiny is undefined. In view of the results of the experiment with very strong peracetic acid these are probably destroyed into substances which are resinified for the main part.

Hence we may conclude that the oxidation of the phenol is directed for almost equal parts to ortho and para. In view of the result of an oxidation

of phenol with H_2O_2 in presence of ferric salts whose green colour proves that pyrocatichol is produced, we should be inclined to admit that the oxidation into muconic acid and phenochinone goes via pyrocatichol and hydrochinol.

The following experiment proves that this conception does not hold true.

We have submitted these substances to the action of peracetic acid: 10 gr. of pyrocatechol were dissolved while cooling in 86 gr. of 10.2 % peracetic acid; a very strong colour appears. After some days a solid substance is deposed, which appeared to be muconic acid m.p. 187°: the amount was no more than 1 gr. After the evaporation in vacuo of the peracitic acid a black amorphous residue remained.

By dissolving 5 gr. of pyrocatechol with great precaution (cooling with ice) in 40 gr. of 78 % peracetic acid at first under development of carbonic acid a strong red colour appears, then the liquid is discoloured, while muconic acid is deposed m.p. 187° (1.3 gr.).

The filtrate of the muconic acid is liberated from the acetic and peracetic acid by distilling the latter substances in vacuo; there remains a pale yellow substance which dissolves in ether. When the ether is vaporized, a substance crystallizes, which is gathered, m.p. 286°, not readily dissolving in water, when heated above the meltingpoint it sublimates in long needles m.p. 51°. Aeq. weight (titration) $= 60$ hence the substance is **fumaric acid.**

In the ether a little of the substance with reducing power remains, which with dinitrophenylhydrazine produces a red precipitate that dissolves in sodium carbonate; when heated it is carbonized.

Analyses N 22.4 and 23.2 mean 22.8 %
                 C 45.0 ,, 45.5 ,, 45.3 %
                 H 3.6 ,, 3.5 ,,   3.55 %.

These analyses of an impure substance do not tell us much more than the presence of 9 C-atoms to 4 N-atoms; consequently it is a hydrazone of a substance with 4 C-atoms. However it cannot possibly be a hydrazine of an aldehydic acid, because the necessary oxygen is lacking. The reactions to oxalic and glyoxylic acid were negative.

In a following experiment the proportion of the amount of muconic acid to the formed carbonic acid was determined, as the first indicates the amount of pyrocatechol, which alone has been opened and as the second is a measure of the destructive reaction. 15 gr. of pyrocatechol were added to 80 gr. of 70 % peracetic acid; the CO_2 was absorbed in potassium hydroxide until the development of CO_2 has ceased and the solution has been discoloured. Thus we obtained 4 gr. of muconic acid and 6.36 gr. CO_2. As 4 gr. of muconic acid is aequivalent to 3.1 gr. pyrocatechol, nearly 12 gr. of pyrocatechol have been decomposed in another direction. If we suppose that out of one molecule of pyrocatechol 2 molecules of CO_2 are formed (next to fumaric acid) then 8 gr. of pyrocatechol would have been used for this.

This result proves that the oxidation of pyrocatechol passes only for a small part via the ortho-chinol (20 %) and that consequently the oxidation of phenol can hardly pass over the pyrocatechol, because the first is converted for 36 % into muconic acid. *So phenol is a much better starting-point than pyrocatechol for the preparation of muconic acid.*

Consequently the formation of muconic acid out of phenol must take place as follows: An oxidation takes place at the C-atom which carries the phenolic hydroxylgroup and at the ortho C-atom. Probably the first product of oxidation passes via ortho-chinone into muconic acid.

Then the oxidation of hydrochinol was examined. 10 gr. of hydrochinol were dissolved in 86 gr. 10.2 % peracetic, acid; very soon chinhydron is deposed, totally 7.8 gr. Thus for about 40 % an oxidation of the hydrochinol to chinone takes place, which combines with the equivalent amount of unchanged hydrochinol and in this condition remains inert towards the diluted peracetic acid.

As phenol in phenochinon is protected against oxidation, this is also the case of the still more easily attackable hydrochinol in the chinhydron.

However, chinhydron is not proof against very concentrated peracetic acid. 5 gr. of hydrochinol added to 50 gr. 35 % peracetic acid produces at first a precipitate of chinhydron that redissolves very slowly. After 10 days the solution is discouloured; no cooling was needed. 1.5 gr. of a white substance is deposed. m.p. 286° aeq. weight 60. When heated above the meltingpoint a sublimate is formed: **fumaric acid.**

From the filtrate the acetic acid is vaporized in vacuo: A mixture remains which is easily soluble in water, has an acid reaction and an equivalent acid number of 64, probably essentially maleïnic acid. It produces a precipitate with $CaCl_2$, soluble in acetic acid. By distillation of a part an abundant sublimate of maleïnic acid-andhydride is obtained, which consequently proves the presence of maleïnic acid. Another part produces with dinitrophenyl-hydrazine in hydrochloric acid solution a precipitate which carbonizes at 162°—165°.

The analysis of this substance gave an average of $C = 45.5 \%$, $H = 4.5 \%$, $N = 18.5 \%$, $O = 32.5 \%$; the proportion between C and N 11 : 4 proves that it is a hydrazone of a substance with 6 C-atoms, the amount of O-atoms is equal to 6, from which 4 belong to the two nitrogroups. Probably this substance is a hydrazone of an aldo- or keto-carbonic acid, as a phase of oxidation before the formation of maleïnic acid and fumaric acid.

Thus the oxidation of the hydrochinol gives in the beginning essentially p-chinone, which combines with unattacked hydrochinol, forming the much less easily oxidable chinhydron. Then this is slowly further oxidized, whereby one of the CH groups, which are all in ortho-position to the CO group is attacked. The molecule is broken up, which moreover causes the production of maleïnic acid by the side of fumaric acid.

It throws a light upon the oxidation of phenol in as much as here no hydrochinol can be formed; since in that case we should find it in the form of chinhydron.

So the oxidation of phenol directed to para produces (perhaps via a possible additionproduct) as first tangible product, parachinon, which is separated in the form of relatively stable phenochinone.

With this the course of the oxidation of phenol with peracetic acid is explained in great lines. It can be compared with the substitutionreactions of phenol, e.g. the nitration.... here too the same ortho and para directive action of the hydroxyl group can be observed.

Whereas however with the substitutionreaction after the first phase, which I should like to call the addition-phase, the benzene-ring redresses itself, this is not the case with the oxidation-reaction.

The oxidation carries through — instead of a orthosubstitutionproduct we get cis-cis-muconic acid, instead of the para-isomer the parachinone (resp. phenochinone).
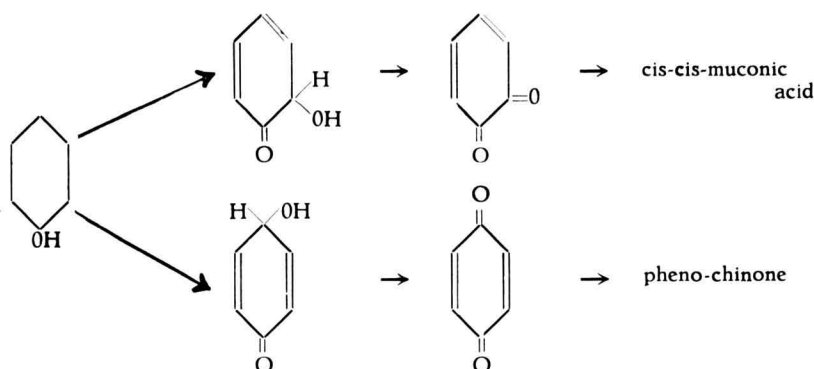
There remains to consider how the fumaric acid can be formed as destructionproduct of the benzene-ring, while one can exclusively expect maleïnic acid. We have proved that maleïnic acid is inert towards peracetic acid. When one dissolves maleïnic acid in 10 % peracetic acid and lets the solution at rest for about ten days, no reaction is produced and after vaporizing the reagent, there remains pure maleïnic acid m.p. 130°.

Neither is muconic acid (m.p. 187°) changed by peracetic acid; moreover one would expect one of the tartaric acids by the side of oxalic acid.

As oxalic acid has never been found, the once found muconic acid is not further destroyed. So one must state that the fumaric acid is formed at the moment that the benzene-ring — resp. chinoidic oxidation-products formed thereof — are attacked. The maleïnic acid can be produced by simple splitting of the para-chinone.

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