Huygens Institute - Royal Netherlands Academy of Arts and Sciences (KNAW)

For d we find the same impossibility : now, the part represented by a straight line must pass through 3 of the points $P_1, \ldots, P_n$, while here on the same surface Φ no intersection in *two* points can occur.

It is therefore evident that of none of the degeneracies a part can pass through *one* of the base-points $P_1, \ldots, P_n$. Through an arbitrary point P_1' in Σ' no bitangent of Φ'_J passes. All the bitangents are therefore lying in $(30-n)$ separate bitangent planes.

The surface itself must be a *cone*.

Chemistry. — "*The photo-oxidation of alcohol with the co-operation of ketones. Contribution to the knowledge of the photochemical phenomena.*" II. By Prof. J. BÖESEKEN and Dr. W. D. COHEN.

(Communicated in the meeting of March 25, 1916).

At the meeting of 31 Oct. 1914 some particulars were communicated by us as to this reaction; since then we have made a closer study of the same and a few important results thereof are found in the dissertation of one of us[1]).

The reaction scheme:

2 ketone $+$ alcohol $=$ pinakon $+$ aldehyde-(ketone),

deduced from comparative velocity measurements with increasing quantities of alcohol could be confirmed in various ways.

First of all it was demonstrated that in this reaction the aliphatic alcohol was converted quantitatively into aldehyde (ketone, respectively) and not into the correlated aliphatic pinacone.

The acetone obtained in the reaction:

$$2 \ C_6H_5COC_6H_5 + CH_3CHOHCH_3 = [(C_6H_5)_2C(OH)]_2 + (CH_3)_2CO$$

was thus weighed in the form of the p-nitrophenylhydrazone and the *cyclo*hexanone formed in the reaction:

$$2 \ C_6H_5COC_6H_5 + C_6H_{11}OH \ (cyclohexanol) = [(C_6H_5)_2COH]_2 + C_6H_{10}O,$$

was determined by the "oxime method".

That, in the photo-oxidation of aromatic alcohols, the said reaction scheme was also correct was proved as follows:

If the reaction had taken place according to the equation:

$$C_6H_5COC_6H_5 + C_6H_5CHOHC_6H_5 = [(C_6H_5)_2 \ C(OH)]_2$$

which also would have been in harmony with the unimolecular course of the reaction, then when taking the two following mixtures:

---

[1]) Dissertation W. D. COHEN, Delft 1915.

$$ClC_6H_4COC_6H_5 + C_6H_5CHOHC_6H_5 \quad \text{and}$$
$$C_6H_5COC_6H_5 + Cl . C_6H_4CHOHC_6H_5$$
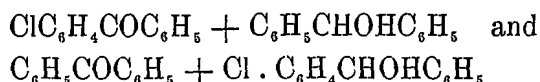
one and the same monochlorobenzopinacone ought to have been formed.

If, on the other hand, the reactions were as stated above, very different products ought to be obtained in each case.

Indeed there was obtained in the first case a chlorine containing pinacone, the chlorine content of which certainly was not so high as that calculated for a dichlorobenzopinacone [this, however, is self-evident because the benzophenone obtained in the reaction from the benzohydrol must be converted together with some unchanged benzhydrol into the ordinary benzopinacone] but still much higher than that calculated for the monochloro compound.

In the second case a pinacone mixture containing but little chlorine was obtained; this also is in full agreement with what was to be expected, as first the chlorobenzophenone formed is at the start present in small quantities only and, secondly, it is converted into the correlated pinacone slower than the benzophenone itself.

From the progressive change of the reaction, as proved by different ways, it thus follows that *both* hydrogen atoms of the alcohol are rendered active.

A fortunate incident subsequently enabled us to further elucidate the course of the reaction.

During the illumination of solutions of terephthalophenone and of *iso*phthalophenone in different alcohols a very distinct yellow coloration was observed. In the beginning this colour disappeared on shaking the tube. When the coloration persisted on shaking, the liquid could still be decolorized by allowing the air to enter into the reaction mixture. Hence, it was obvious to attribute the decolorization to oxidation; that in this case the oxygen played indeed an important role could be shown by placing the mixture (freed from oxygen by boiling) in a space filled with oxygen-free nitrogen; on exposure to ordinary day-light the contents of the tube turned immediately yellow; if now a trace of air was admitted, the liquid got again decolorized.

In order to show the oxidation still more distinctly, the saturated solution of terephthalophenone with a slight excess of the ketone was placed in a vessel furnished with a doubly bent tube which dipped into mercury; the space above the liquid was filled with air. On illumination, the mercury gradually rose and the small excess of terephthalophenone did not perceptibly dissolve. This only took

place after the oxygen had' been consumed and the colour had almost completely faded.

After some time, beside the residual terephthalophenone another non-coloured substance began to deposit; this went on until the original terephthalophenone had entirely disappeared and the liquid again was almost quite decolorized.

To judge from the molecular weight, the colour reaction with potassium hydroxide (to which we will refer later) and the decomposition on heating the new product consisted of the terephthalophenopinacone.

When we place the yellow solution in the dark it keeps unchanged for months; if, however, air is admitted it is also very rapidly decolorized.

Finally it should be remarked that if an inert solvent but no alcohol is present, no yellow coloration sets in, so that the alcohol is a necessary condition for this colour reaction. Taking into consideration our previous results we may conclude from the foregoing:

1st. The ketone absorbs a part of the violet rays.

2nd. The following photo-reaction takes place:

terephthalophenone + alcohol + little light = yellow substance in which the two hydrogen atoms forming part of the alcohol molecule are rendered active.

This substance is permanent in the dark but is decomposed by oxygen as follows:'

yellow substance + oxygen = terephthalophenone + aldehyde
(ketone) + H_2O.
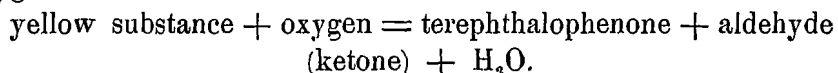
3rd. If the yellow substance is further illuminated it is converted according to the reaction:

yellow substance + much light = terephthalophenopinacone +
+ aldehyde (ketone).
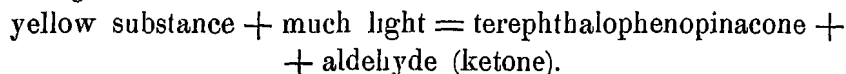
After this elucidation it was only natural to ascertain whether in the case of the other ketones, where the yellow colour is not so pronounced or could not even be observed, the progressive change was the same.

Indeed it could be ascertained that if reduction to pinacone did occur, there could always be noticed absorption of oxygen should this gas be present.

To demonstrate this, a little apparatus was employed consisting of a vessel of 20 cm. capacity in which was placed a hollow stirrer with T-piece and opening. By the rotation of the stirrer the gas from the gaseous space was forced through the liquid and kept this saturated with air. The stirrer was also connected. air-tight with the

axis of a mercury seal that could be rotated with a little motor whilst the gaseous space was connected with a mercury manometer by means of a capillary.

In this manner, not only the oxidation could be ascertained but also its velocity could be measured.

A small vertical plate placed perpendicularly to the wall and projecting just above the surface of the liquid served to keep the surface tranquil; a similar little plate was also found in the small mercury reservoir of the seal causing the mercury surface to keep in the horizontal position.

The reduction to pinacone and the oxidation of the alcohol to aldehyde and water seem to be inseparately connected with each other; a priori this is not necessarily so. We may conceive that the H is rendered active in such a manner that it combines with oxygen without being yet capable of attacking the ketone, and conversely.

As these two reactions probably take place together, the action of the CO-group on the H of the alcohols, which leads to an activity towards the O of the air as well as to that of the ketone, must be attributed to a same cause.

Only there is a difference and that is that the oxidation reaction can proceed further without the assistance of light, *seemingly because this is a catalytic reaction*, whereas the pinacone formation requires the continuous assistance of the light energy.

From our previous communication it appears that there are a number of ketones, which, although they powerfully absorb the light, are not at all, or at least not perceptibly, capable of activating the alcoholic hydrogen. [1]

Many of these ketones may, however, be conveniently reduced by other means, the non-occurrence of the photo-reduction must, therefore, be looked for in the particularly unfavourable condition of the CO-group in connexion with the influence of other groups in regard to the light.

The condition of the CO-group in the ketone molecule as determined by all surrounding molecules will regulate the power of rendering active alcoholic hydrogen atoms. Moreover, a reciprocal reaction between *two* ketone molecules and one alcohol molecule must be able to take place.

The catalytic alcohol-oxidation with the co-operation of the CO-

---

[1] It is presumably a quantitative difference; *o*-methyl-benzophenone does it slowly so that we have just been able to show it by means of the oxidation reaction; fluorenone acts much slower still

group rendered active by exposure to light, as found by us, now enables us to obtain a series of aldehydes in a perfectly neutral medium.

Here, however, it must be observed that the alcohol should not cause a hindrance.

It appeared for instance that citronellol, although a primary alcohol with a double bond far removed from the OH-group was not oxidised; this now must be attributed to a disturbing influence exerted by the alcohol on the active light.

If we place this alcohol in the jacket of the mantle tube (see previous communication), it also retards the reduction of benzophenone by ordinary alcohol in the inner tube.

Even with strong sun-light in the spring the velocity of the reaction is but small: this can only be remedied by enlarging the surface illuminated. If we wish to become independent of the sun-light powerful mercury lamps will have to be used with the reaction mass in a jacket round the arc light.

For practical purposes we do not consider the photo-reaction to be of much importance just yet, but from a theoretical point of view it is so all the more.

This now may appear from the following points:

1st. It has been shown that, among all other primary and secondary, saturated alcohols, the methyl alcohol occupies a special place because reaction with benzophenone and its derivatives takes place much slower (see previous communication).

This is based on a lesser activity of the H-atoms of the alcohol towards the oxygen and not, as in the case of citronellol, to an absorption of active rays.

Therefore, we can understand that also the physiological action of this alcohol must be different from that of its analogues. This difference has been found with the human being as well as with *penicillium glaucum*.

2nd. When we consider the succession of the photo-reactions which from the mixture of aromatic ketone and alcohol lead to pinacone and aldehyde we find some resemblance to the assimilation process.

Of the latter we can very roughly conceive the following image:

I. (chlorophyllogen + protoplasm) + little light = (chlorophyll + protoplasm).

II. (chlorophyll + protoplasm + carbon dioxide) + more light = (chlorophyll + protoplasm + formaldehyde) + O_2.

III. chlorophyll + protoplasm + formaldehyde = chlorophyll ? + protoplasm + sugar etc.

The assimilation process is undoubtedly much more intricate than the one studied by us for instance on account of the not as yet surveyable endo-enzymic action of the living protoplast, but here also we have first (I) a transformation of a definite system by means of a slight light intensity into another photo-active condition, subsequently (II) a photo-reaction requiring more light.

Part (III), the formation of sugar or amylum is a synthesis which is caused presumably by other enzymes and has a purely catalytic character.

The fact that here are formed optically active compounds from carbon dioxide will presumably be due more to the asymmetric construction of the protoplasm than to that of the chlorophyll. Of the asymmetry of the chlorophyll nothing is known. It is possible because phytol, the unsaturated alcohol in the chlorophyll, is probably built up asymmetrically, but as the generation of sugar from formaldehyde is more of a protoplasm function than an accelerating effect of chlorophyll, it is more rational to also look to the protoplasm for the cause of the asymmetry of the amylum obtained.

In the photo-process studied by us lies, moreover, the possibility for the realisation of a simple asymmetrically-proceeding photo-reaction.

Starting from the system:

optically active ketone + racemic alcohol = pinacone + aldehyde, we may expect that one of the optic antipodes will be oxidised to aldehyde more rapidly than the other. Whether this view is correct will have to be settled experimentally.

3rd. The significance of the catalytic oxidation of the alcohols for the better understanding of the catalytic reactions particularly amounts to this, that we get here very plainly the impression that there is wanted a continuous, though it may be a small, supply of energy to keep the catalysis going:

Only the ketone-alcohol mixture energetically activated by the light, namely the just mentioned yellow substance is capable of taking up the oxygen and if we wish to proceed with the alcohol oxidation we must continuously take care to promote this activation.

The reaction :

alcohol + oxygen = H_2O + aldehyde (ketone)

is thus kept active by a photo-action in the CO-group of the aromatic ketone.

If we compare this with the effects of platinum or palladium this

can be explained, according to the investigations of WIELAND, in a perfectly analogous manner.

Palladium is capable of withdrawing hydrogen from an alcohol and this absorbed and activated hydrogen is then attacked by the oxygen.

In the phota-reaction the case is in reality still simpler and purer.

With the co-operation of definite rays of light, the ketone is capable, if not of actually withdrawing the H, of modifying the same (in some cases perceptible by the yellow colour).

Which practically will amount to the same thing, for as soon as we want to get a conception as to the change of the H, a form must be given to it in which either the position of the atoms or that of the electrons must be considered as modified.

The photo-active H can now form water with the oxygen just like the Palladium-active hydrogen can do this.

We have tried whether the element H_2 might also be rendered active by means of the system Ketone + light, but this did not succeed.

From the experiments of CIAMICIAN and SILBER and also from our own we must, however, conclude that a large variety of hydrogen compounds is certainly capable of it.

In consequence of our observations as to the activation of the alcoholic hydrogen the following question still arose, in connexion with the catalytic phenomena.

We can conceive ethyl alcohol to be built up of ether and water and there are indications that in the system:

$$(C_2H_5)_2O + H_2O = 2C_2H_5OH$$

the alcohol at the ordinary temperature is more stable than the mixture of ether and water.

If this is so, the formation of alcohol under the influence of definite catalysts ought to be capable of demonstration.

Now, we have first of all tried the effect of illumination on benzophenone in absolutely dry ether; no action had taken place in the time that it was converted with absolute alcohol, completely into pinacone.

We remind the reader that water exerted a very retarding influence on the photo-reaction.

- On illuminating a solution of benzophenone in *moist ether* a liberal formation of pinacone and aldehyde was noticed.

$$4C_6H_5COC_6H_5 + (C_2H_5)_2O + H_2O = 2[(C_6H_5)_2COH]_2 + 2C_2H_4O$$
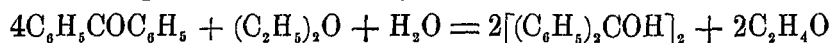
Hence, the photo-reaction has here induced the alcohol formation and this notwithstanding the retarding action of water which at the commencement was present in considerable quantities.

The experimental details will be published elsewhere.

Chemistry. — "*The hydrogen-ion-concentration of some complex polyhydroxyborate solutions,*" By Prof. J. Böeseken and A. H. Kerstjens.

(Communicated in the meeting of March 25, 1916).

The relation found by one of us between the influence exerted by a number of polyhydroxy-compounds on the electric conductivity of boric acid, (rendering it possible to get some more information as to the configuration of these compounds) made it desirable to further trace the cause of the change in conductivity. From what was found (which, moreover, was already known from observations of other workers) boric acid frequently becomes a more powerful acid, and the increase in the concentration of the H-ions must, therefore, be considered as being the most important cause of the exaltation in conductivity.

Slight decreases in conductivity have, however, also been noticed which may then be attributed on the one hand to the formation of complexions with small migration constants, on the other hand to a greater viscosity of the medium.

We have now in the first place made it our task to determine the H-ion concentration of a few diverging cases and to compare these values with those which could be calculated from the determinations of the conductivity.

The H-ion concentration was deduced from the electromotoric force of a concentration chain which was determined according to the compensation method of Poggendorf with the capillary electrometer of Lippmann as-zero-instrument.

The complex boric acid solution investigated by us formed part of the concentration chain:

. H_2 (p $= 1$ atm.) | $C_{H\cdot}$ | satur. KCl | Hg_2Cl_2 in 0.1 n. KCl | Hg .
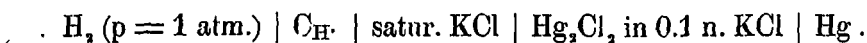
In view of the small H-ion concentration the vessel, containing