**Chemistry.** — *The Light Oxydation of Alcohols as Contribution to the Knowledge of the Photo-Chemical Phenomena.* By J. Böeseken and S. L. Langedijk.

§ 1. The researches made by one of us for some ten years with collaboration of W. D. Cohen [1]) and H. D. Muller [2]), had yielded the result that there are a number of aromatic mono- and aliphatic α-diketones which are sensitive to light in the extreme part of the visible spectrum. Exposed to the light they can oxidize a number of hydrogen compounds, especially the primary and secondary alcohols, to the corresponding aldehydes and ketones, in which they themselves are reduced to pinakones, e.g.:

$$2\,C_6H_5\,COC_6H_5 \text{ (illumination)} + C_2H_5OH \rightarrow [(C_6H_5)_2\,COH]_2 + C_2H_4O.$$
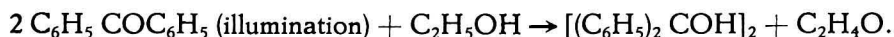
If there is sufficient oxygen present, an oxidation takes place of the alcohol to the aldehyde (ketone), in which the aromatic ketone remains seemingly unchanged, thus playing the part of photo-catalyst.

It then appeared that the quantities of pinakone in the first case and the consumed oxygen in the second case were equivalent, when for the rest the circumstances were the same, i. e. that two mol. of pinakone were formed in the same time that one mol. of oxygen was consumed.

If further appeared that already at moderate concentration the velocity of reaction became little dependent on the concentration of the ketone, that it was proportional to the concentration of the alcohol, and — when the circumstances were chosen the same for the rest — proportional to the *square* of the light intensity. With a view to this a scheme of reaction was drawn up by one of us, in which it was assumed that the velocity of formation was *measured* of a compound from two activated benzophenon-molecules with one mol. of alcohol:

2 Photo-active ketone $+$ 1 alcohol $=$ (photo-active ketone)$_2$ alcohol, which compound could then react with much greater velocity in two directions according as oxygen was present or not:

(photo-active ketone)$_2$ alcohol $\rightarrow$ pinakone $+$ aldehyde
2 ,, $+ O_2 \rightarrow 4$ ketone $+ 2$ aldehyde $+ H_2O$.
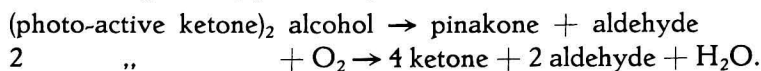
In order to be able to give and idea of the course of conversion, we must give an account of the succession of the processes:

If a certain quantity of ketone is struck by the light, the intensity of

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[1]) W. D. Cohen, Proefschrift, Delft, 1915.
[2]) Böeseken, Recueil. Trav. Chim., **40**, 433 (1921).

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the light will be unequally distributed in consequence of the absorption of the light in the vessel, and it will diminish from I_0 to $I_0 e^{-\varkappa c x}$, dependent on the absorption coefficient of the ketone ($\varkappa$) and on its concentration (c) over the cross-section of the vessel (x). Accordingly at the moment of the illumination there will be a number of active molecules, the concentration of which decreases from the light side to the dark side according to this law.

Now the question may be raised, what happens immediately after this activation? If these molecules act as perfect mirrors, i.e. if they send back the light energy with the same velocity, we could only speak of reflecting or scattering, and the concentration of the active molecules would remain insignificant. The fact that in the absence of appreciable reflection and scattering a vigorous absorption is observed, suggests that the activated molecules have time to transfer their activity to themselves or to other molecules.

A. If we asssume in the first place that this time is very short, they will only be able to bring about this transference at the place itself or very close to the place of their activation. The concentration in an arbitrary layer of light in active benzophenone molecules may then be calculated as follows. By the illumination a number of active ketone molecules is formed proportional to the quantity of light present there. If S is the illuminated surface, the quantity is:

$$= K_1 \, S \, I_0 \, e^{-\varkappa c x} \, . \, \varkappa c \, dx.$$

Part of these will be converted; if we assume this to be a monomolecular reaction (that we may, therefore, disregard collisions of equal molecules) the number of disappearing molecules $= K_2 \, c_{\text{active-ketone}} \, S dx$.

A stationary state will result, when these two reactions are in equilibrium; from this ensues that in every layer of light the concentration of the active ketone mol. $= K_1 \, I_0 \, e^{-\varkappa c x} \, \varkappa x$. These active ketone molecules now get secondarily in contact with alcohol molecules, in which the ternary photoactive compound (see further) originates:

$$\frac{d \, [\text{tern. comp.}]}{dt} = K_2 \, c^2_{\text{act. ket.}} \, . \, c_{\text{alcohol}} = K_2 \, K_1^2 \, I_0^2 \, e^{-2\varkappa \, cx} \, . \, \varkappa^2 c^2 \, . \, c_{\text{alcohol}}$$

From this the total quantity of this compound in the layer can be calculated by multiplication by $S \, dx$, and then by integration the total quantity in the vessel is:

$$\int_0^x S \, K_2 \, K_1^2 \, I_0^2 \, e^{-2\varkappa cx} \, \varkappa^2 c^2 \, c_{\text{alcohol}} \, . \, dx = \frac{1}{2} \, S \, K_2 \, K_1^2 \, I_0^2 \, (1 - e^{-2\varkappa cx}) \, \varkappa \, c \, c_{\text{alcohol}}$$

The concrete increase $= \dfrac{d[\text{comp.}]}{dt} = \dfrac{1}{2} \, \dfrac{K_2 \, K_1^2}{x} \, I_0^2 \, (1 - e^{-2\varkappa cx}) \, \varkappa \, c \, c_{\text{alcohol}} \, .$

B. If we assume that the activated benzophenone molecules lose their activity comparatively slowly, so that in a thin layer and at not too

low temperature we may assume that they have time to spread evenly through the reaction space without having lost much of their activity, a stationary state will have established itself after a short space of time, which may be represented by:

$$\int_0^x K_1 \, S \, I_0 \, e^{-\varkappa c x} . \, \varkappa c \, dx = K_1 \, I_0 \, (1-e^{-\varkappa c x}) \, S = K_2 \, c_{\text{active mol.}} \, . \, x \, . \, S.$$

or

$$c_{\text{act. mol.}} = \frac{K_1}{K_2 \, . \, x} \, I_0 \, (1-e^{-\varkappa c x}).$$

If we, therefore, suppose a sufficient duration for the light-active molecules, and if we choose a small and equal thickness of the layer, since this is necessary for a sufficient absorption of oxygen, we may use for concentration of the active molecules the expression: $\frac{K}{x} \, I_0 \, (1-e^{-\varkappa c x})$, and express the velocity reaction by:

$$\frac{d \, [\text{active comp.}]}{dt} = \frac{K^2 \, I_0^2}{x^2} \, (1-e^{-\varkappa c x})^2 \, . \, c_{\text{alcohol}} \, .$$

Whatever image we may use here, always the square of the light intensity appears; a choice between the two views can only be made by the determination of the reaction velocity under different cirumstances.

§ 2. *The photo-active region.* It had already been rendered probable by COHEN that the photo-active region lies in the extreme visible violet and that the ultra violet, for so far as the region of the mercury lines occurring in it is concerned, was inactive.

On absorption of the visible light by a solution of nitroso dimethylaniline, no reaction could be observed of this light in quartz tubes. For the rest there remained much uncertainty about the extension of the photo-active region.

One of us has defined this active area more closely with H. D. MULLER in the following way. We made use of another reaction, which, however, likewise ensues from the formation of the ternary compound: (photoketone)$_2$ alcohol.

If an alcoholic solution of $Hg \, Cl_2 + (NH_4)_2 \, C_2O_4$ is illuminated in the presence of the above-mentioned ketones, $Hg \, Cl$ is deposited in the sunlight and in the light of the mercury lamp.
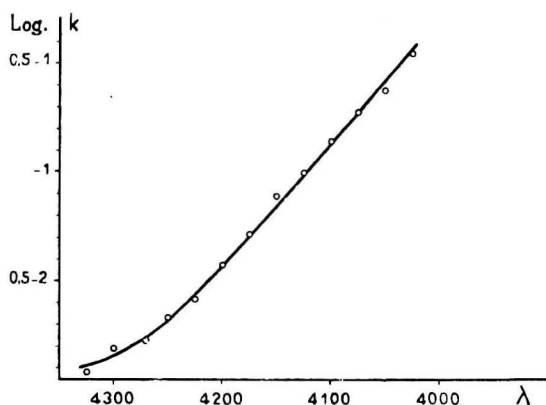
We then laid a series of capillary tubes filled with this solution, under the microscope, and illuminated them by means of a spectrum obtained by the aid of a strong PHILIPS microburner.

It could then clearly be observed that in the tube which was in the extreme violet between 400 and 410 $\mu\mu$, the first HgCl crystals appeared;

not until some days later were there also seen crystals on either side of this tube, both to the side of the red and to that of the ultra-violet in a greatly decreasing degree. These crystals being of about the same size and the tubes having the same diameter, their number was an approximate measure of the converted quantity of substance. Though this number decreases exceedingly rapidly, we may yet conclude that the photo-active region is not confined to a few light vibrations.

Then the question suggested itself if this region of photo-activity with a clearly-marked top coincided with a region of general absorption.

As the Technical University is not fully equipped with apparatus for accurate determinations, one of us has called in the hospitality of the physical laboratory at Utrecht, which is under the direction of Prof. ORNSTEIN. Through the very kind assistance met with there, he has succeeded in defining the whole area of absorption of some ketones both in the visible light and the ultra violet part of the spectrum adjoining it.

In this there was not found the slightest indication of an absorption top in the violet part. We are here in the ascending part of the region of absorption, but with the three investigated ketones we are very far from the top, which lies in the ultra violet part of the spectrum, where we have not met with any reaction. The fact, indeed, that the photo-active region is narrowly limited indicates that it is quite surrounded by the region of total absorption.

We see that part of the light energy, and undoubtedly only a very small part, can be applied for this oxidation reaction, hence that the photo-chemical efficiency is small. It is certain that when the light is thought divided in separate vibrations, there are some among these vibrations that possess a very high efficiency; the more we are, however, struck then with the slight efficiency of the light vibrations from the rest of the absorption region.

If the photo-active region were confined to very few light vibrations, we might imagine the case that the photo absorption top was so sharp that it was not observed in the determination of the total absorption region. The experiments with the capillaries show, however, that the photo active region in question is not to exceedingly narrow.

It is possible that one single ray of light possesses an efficiency of 100 $^0/_0$, and it would certainly be of great importance to refine the means of investigation to such an extent that this too could be found.

It follows from our investigations and those by COHEN that the tops of the photo-active regions for different ketones lie "in the neighbourhood" of the mercury lines in the violet, and that these regions certainly overlap for an important part, (see below). It is, however, a priori probable that the real top occupies a separate place in the spectrum for every ketone. For the rest the general absorption is very sensitive to admixtures; it was found by us that an alcoholic solution of the ketones yielded a spectrum which was turned more towards the red than a solution in petroleum ether.

When the question is now considered what happens with the rest of the absorbed energy, it is undoubtedly conceivable that *other chemical reactions* may be started by it, e.g.: $C_6H_5COC_6H_5 + C_2H_5OH \rightarrow$ $\rightarrow C_6H_5COO_2H_5 + C_6H_6$, which then take place somewhere in the ultraviolet absorption region, etc. Under the circumstances chosen by us, the rest of this energy is probably entirely converted to heat.

With somewhat complicated molecules no theoretical light efficiency can in general be expected throughout the whole absorption region, nor is this, certainly, the case with the assimilation process. Here, too, the photochemical region is encompassed by the general absorption region of the chlorophyll. The maximum efficiency is not reached at the characteristic top in the red, $(645-670 \, \mu\mu)$, it lies probably more in the yellow between $570-645 \, \mu\mu$, hence here (O. WARBURG and E. NEGELEIN Z. phys. Ch. 102, 235 (1922)) past the top.

§ 3. Some mixtures of ketones in alcoholic solution were illuminated by W. D. COHEN in order to examine whether disturbances appeared then, and if so what disturbances. Because with somewhat considerable concentration of the ketone the reaction velocity seemed to be independent of this concentration, it was at first expected that the two reactions would not interfere with each other. This appeared to be by no means the case.

If we consider the velocity of formation of the pinakones:

$$- \frac{d\,[\text{ternary comp.}]}{dt} = + \frac{d\,[\text{pinakone}]}{dt} = \left[\frac{I_0 K}{x} (1 - e^{-\varkappa cx}) \right]^2 c_{\text{alcohol}}$$

then with somewhat considerably concentration and with *perfect specific absorption* the increase of the concentration will really have little influence on the velocity of formation of each pinakone separately, as $(1 - e^{-\varkappa cx})$ rapidly approaches to the unit.

When they are mixed, however, and when the absorption regions coincide at the places of the photo-activity, the two ketones will divide this light according to their power of absorption and their concentration.

One ketone will partly be in the path of light of another ketone, so that we then might speak of an *interior filter action*. The law of this,

formulated by LUTHER and WEIGERT, Z. Phys. Ch. **53**, 408 (1905), has been applied by one of us (LANGEDIJK) as follows:

If a vessel with two substances in the same solvent with the concentrations c_A and c_B is exposed to monochromatic light, the absorption coefficients being $\varkappa_A$ and $\varkappa_B$, the intensity of the light after having traversed a layer dx is diminished by the amount:

$$- dI = (\varkappa_A c_A + \varkappa_B c_B)\, I\, dx$$

$$\frac{dI}{I} = - (\varkappa_A c_A + \varkappa_B c_B)\, dx$$

$$ln\, I = - (\varkappa_A c_A + \varkappa_B c_B)\, x + C$$

$$I = C' . e^{-(\varkappa_A\ c_A + \varkappa_B\ c_B) x}.$$

For $x = 0$ $I = I_0$ hence $C' = I_0$, from which follows:

$$I = I_0\, e^{-(\varkappa_A\ c_A + \varkappa_B\ c_B) x}.$$

Then the total absorption, after having traversed a layer x, is then [1]:

$$H = I_0 \left[1 - e^{-(\varkappa_A\ c_A + \varkappa_B\ c_B) x}\right].$$

If we further call H_A the quantity of light absorbed by A, and H_B that absorbed by B, the following equation is valid for a thin layer:

$$dH = dH_A + dH_B = - dI = (\varkappa_A c_A + \varkappa_B c_B)\, I . dx$$

and we may think this distributed in this very thin layer as follows:

$$dH_A = \varkappa_A c_A I\, dx \quad \text{and} \quad dH_B = \varkappa_B c_B I\, dx.$$

Now $I\, dx = - \dfrac{dI}{\varkappa_A\ c_A + \varkappa_B\ c_B}$

$$dH_A = - \frac{\varkappa_A\ c_A}{\varkappa_A\ c_A + \varkappa_B\ c_B}\, dI \quad \text{and} \quad dH_B = - \frac{\varkappa_B\ c_B}{\varkappa_A\ c_A + \varkappa_B\ c_B}\, dI$$

If these values are integrated, we get as above:

$$H_A = \frac{\varkappa_A\ c_A}{\varkappa_A\ c_A + \varkappa_B\ c_B}\, I_0 \left[1 - e^{-(\varkappa_A\ c_A + \varkappa_B\ c_B) x}\right]$$

$$H_B = \frac{\varkappa_B\ c_B}{\varkappa_A\ c_A + \varkappa_B\ c_B}\, I_0 \left[1 - e^{-(\varkappa_A\ c_A + \varkappa_B\ c_B) x}\right].$$

If, therefore, there are some substances present in a solution, they divide the absorbed light of a definite wave-length — hence also the photo-active light — in proportion to the products of their concentrations and absorption coefficients.

Since with the reaction velocities of our ketone reductions the squares of this value come into play, it is clear why COHEN observed such strong

[1] This derivation of the total absorption in the presence of two (and more) substances, has already been given by PESKOW, Journ. Russ. Chem. Ges. **47**, 918(1915), Journ. Phys. Chem. **21**, 382 (1917).

disturbances in mixtures of benzophenone with small quantities of strongly absorbent substances. In fluorenone-benzophenone mixtures he has actually found values that are almost in accordance with the values calculated by us from the known absorption coefficients according to the derivation given above.

In this it should, of course, be taken into consideration that this law has been derived for monochromatic light, and that the photo-chemical reaction is caused by a region of varying activity, and the light efficiency is different there for every ray of light.
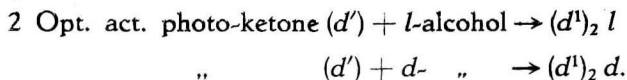
This filter action is of very great importance from a theoretical as well as from a practical point of view.

If we choose the assimilation process, it follows from the above that the presence of small quantities of pigments, which take away the active light in the cell at the place of the chlorophyll grains, must constitute a very efficient protection, it is very well possible that a regulating influence is exerted by this.

Also the formation of small quantities of pigments in our skin can considerably temper the too vigorous action of the direct sunlight; they form a powerful light screen against these actinic rays.

Of the substances which are used for dyeing clothes it is well-known how sensitive many of them are to direct irradiation, and it is, therefore, of great importance, led by a systematic investigation of the photo-active regions, to try and find substances which, little coloured themselves, show all the same a vigorous absorption in those regions.

§ 4. Finally we have tried to make use of this light-reaction to reach the decomposition of optical antipodes. If we really measure the velocity of formation of the ternary compound, and if we start from a ketone which is at the same time photo-active and optically active, a difference may be expected in the velocity with which the levo-rotatory and the dextro-rotatory component of a racemic alcohol combines with it to a ternary compound:

$$2 \text{ Opt. act. photo-ketone } (d') + l\text{-alcohol} \rightarrow (d^1)_2 \, l$$

$$\text{,,} \qquad (d') + d\text{-} \quad \text{,,} \quad \rightarrow (d^1)_2 \, d.$$

The quantities of these compounds are not perfectly the same.

Besides, the ternary compounds formed can oxidize with different velocities, because these substances differ from each other in every respect.

Hence on distillation of the alcohol, a small excess of one of the other components will be found.

The preparation of a photo-active and optically active ketone was attended with a good many difficulties; a product that ultimately was found satisfactory, was the l-menthyl-ester of benzophenone-p-carbonic acid: $C_6H_5\text{-}COC_6H_4COO\text{-}l\text{-menthyl}$.

This was placed in a solution of rac. phenyl-ethyl-carbinol (1 gr. in

20 cc.) and illuminated for 30 hours in a light-thermostat with 30 volts and 3.5 ampères — the oxygen absorption being 0.012 cc. per minute. The alcohol distilled off exhibited *no rotation*. The experiment was repeated with methyl-ethyl carbinol. There were absorbed 0.14 cc. O_2 per minute. The carefully fractionated methyl-ethyl carbinol showed faint levo-rotation at 60 volts and 4.1 Ampères after 100 hours' illumination, in which, therefore, 6×0.14 litres $O_2 = 0.841$ had been absorbed, equivalent to 2.5 grammes of alcohol. In a 2 dm. tube this amounted to $-0°.04$; a repeated experiment gave $-0°.03$. Though the amount is very small, it is certainly above the error of observation, and we may say with pretty great certainty that in principle a decomposition has been effected by this way.

New points of views are opened in so far that it must be possible that in nature in the presence of compounds at the same time sensitive to light and optically active, new optically active compounds are built up by photo-chemical way.

In the assimilation process the formation of optically active glucose and of amylum is not necessarily connected with the light process. This may be restricted to the activation of the chlorophyllcarbonate to a product of high potential energy, that now further under the influence of enzymatic dark reaction can change into oxygen and into optically active compounds.

Delft, Dec. 1926.