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ments it may be mentioned that the ratio $\text{Cl} : \text{NH}_2$ is very large. The above velocity series must, therefore, be resolved into two parts: OH and NH_2 which cause a great substitution velocity and which are presumably of the same order of magnitude; on the other side the halogens and CH_3 with a lesser velocity, also of the same order of magnitude. A more detailed description of the above experiments will be published in the Recueil.

Oct. '14.

Org. Chem. Lab. University Amsterdam.

Physics. — “*The reduction of aromatic ketones. III. Contribution to the knowledge of the photochemical phenomena.*” By Prof. J. BÖESEKEN and Mr. W. D. COHEN. (Communicated by Prof. A. F. HOLLEMAN).

(Communicated in the meeting of October 31, 1914).

I. *The reduction of the aromatic ketones in a perfectly neutral medium.*

In our former communications ¹⁾ we have shown that the reduction of the aromatic ketones does not proceed any further than to pinacone, which is presumably formed from the primary generated half pinacone molecule by rapid polymerisation. The fact that in an alkaline medium hydrol is always obtained, must be attributed to the rapid transformation of the pinacone, under the influence of the hydroxylions, into an equimolecular mixture of hydrol and ketone, the latter of which can be again reduced to pinacone.

This explanation was confirmed by the study of the reduction of ketones by means of aluminium amalgam.

Here is formed a mixture of pinacone and hydrol; the proportion in which these two substances are formed differs from ketone to ketone and now it appeared that the quantities of hydrol ran strictly parallel to the velocities with which the diverse pinacones are converted into a mixture of ketone and hydrol under the influence of sodium ethoxide.

Hence, aluminium amalgam in 80% alcohol may by no means be considered as a neutral reducing agent.

The only *modus operandi* that gives the necessary guarantee that complete neutrality would prevail during and after the reduction is the action of the aromatic ketone on an alcohol under the cooperation of sunlight. The original intention of this part of the research,

¹⁾ Proc. XVI p. 91 and 962 (1913).

namely the tracing of the progressive change of the reduction, was soon attained by applying this method.

A series of ketones dissolved in a great variety of alcohols and a few other substances, was exposed to sunlight (or to the light of the quartz-lamp); *in all cases where reduction set in, not a trace of hydrol was obtained.*

The ketone was usually quantitatively converted into pinacone; occasionally, namely with benzylalcohol and a prolonged exposure to sunlight a combination of the half pinacone molecule with a group of the benzylalcohol, namely triphenylglycol was obtained as a by-product.¹⁾

When to the alcohol some ethoxide was added hydrol was formed, as was to be fully expected.

Hence, we arrive at the result that in the reduction of aromatic ketones the hydrogen unites exclusively with the oxygen.

The experiments were carried out as follows:

Quantities of 5 grams of the ketone were dissolved in 50 cc of alcohol rendered carefully anhydrous²⁾ and exposed in sealed tubes of common glass to direct sunlight.

The drying of the lower terms was performed by successively boiling with CaO, allowing to remain over metallic calcium at 0°, and distilling; the higher ones were purified by distillation and both were then immediately sealed into the tube together with the ketone. After exposure to the light for some time, during which the course of the reduction could be traced by noticing the deposition of the sparingly soluble pinacone, the tube was opened, the pinacone was filtered off, the filtrate distilled, the residue united with the pinacone and in the distillate the aldehyde or ketone was tested and in some cases determined quantitatively.

The exact details will be published elsewhere by one of us, a few remarks may suffice here.

First of all was investigated the behaviour of benzophenone in regard to methyl, ethyl, *n*-propyl, *sec.*-propyl, *iso*-butyl, *n*-heptyl, *sec.*-octyl and cetylalcohol. The latter only was not attacked, not

¹⁾ This had already been noticed by CIAMICIAN and SILBER (B. 36, 1577 (1903)); the formation thereof is moreover a confirmation of our conception that as the first reaction product the half pinacone molecule is formed.

²⁾ Water acts in this reaction in a remarkable manner as a powerful negative catalyst; in 80% alcohol no reduction takes place after exposure for months, whereas in absolute alcohol in the same conditions, about two grams of pinacone are formed during ten hours' action of sun-light.

even at higher temperatures; the mixture however, was of a fairly strong yellow colour.

The other alcohols reduced the benzophenone in some sunny spring days, with the exception of methylalcohol which required a much longer time.

The research was then continued with allylalcohol, geraniol, *cyclohexanol*, benzylealcohol, phenylmethylalcohol, benzhydrol and cinnamylalcohol. Of these, the saturated alcohols reduced rapidly and quantitatively; the allylalcohol was attacked more slowly with formation of acraldehyde (even after two months' exposure to light, the acraldehyde was unchanged, thus showing that the light alone does not exert a polymerising influence on this mobile substance).

The geraniol was also oxidized very slowly, the cinnamylalcohol remained unaffected (we will refer to this behaviour later).

A few tertiary alcohols were also investigated; it was expected that these would remain unaffected and indeed this was the case with the dimethylethylcarbinol after two months' exposure; during that period, diaethylmethylcarbinol had generated 0,3 gram of pinacone; with methyl-di-n-propylcarbinol the separation of pinacone started after a few days and after two months 0.7 gram had formed.

From this we notice that when the chain becomes longer, the activity of the hydrogen of tertiary alcohols gets enhanced, which enables it, with the cooperation of sun-light, to attack an aromatic ketone; what gets formed from the alcohol has not been investigated by us.

From observations of CIAMICIAN and SILBER¹⁾ it is known that the hydrogen of some hydrocarbons, such as toluene, is already active enough to cause this reduction. We have been able to show that also the hydrogen of the *cyclohexane* is transferred to the ketone, on the other hand, hydrogen itself was not capable of acting.

Besides benzophenone some other ketones — particularly those that were previously subjected by us to the action of aluminium amalgam — were subsequently exposed in alcoholic solution to the light.

Nothing but pinacone was ever obtained, but the phenomena occurring in these photo-reactions induced us to systematically repeat a large part of these purely qualitative observations in such a manner that on using a very simple *modus operandi* a relatively-quantitative result was still obtained.

¹⁾ B. 43. 1537 (1910).

II. *The photo-reaction: ketone + hydrogen = pinacone.*

In order to obtain a relatively-quantitative result we could make use of a constant source of light and allow this to act on the different solutions under the same conditions; for this purpose a small 7 cm. quartz-mercury lamp was at our disposal. Yet we have employed this method but rarely, for instance in continuous dark weather, because on account of the unequal distribution of the light, at most two little tubes could be placed in front of the lamp in such a manner that it might be assumed that they existed under equal conditions.

When it had been ascertained by us that the reduction took place quite as well in ordinary white glass as in quartz, from which it appeared that a very large part of the actinic rays was situated in the visible spectrum, the experiments intended for comparison were carried out as follows:

A number of equally wide tubes of the same kind of glass and having walls of approximately the same thickness were filled with the same quantity of solution, and all placed at the same distance in front of a white screen, which was placed close to a large laboratory window.

In this manner it was attained that the quantity of light that fell in the same time on each solution was practically the same, and perfectly comparable results were thus obtained.

It speaks for itself that even then only the figures of a same experimental series were mutually comparable.¹⁾

A photo-reaction is distinguished from a reaction in the dark by two points.

It is of a lower and frequently of the 0 order in regard to the substance which is being activated and the temperature coefficient is small.²⁾

As we found that the active light was situated in the visible spectrum and that the alcohols do not absorb visible rays, the ketones are in this reaction the sensitive substances, and so we could expect that the quantities of pinacone would be independent of the

¹⁾ Also comp. O. GROSS Z. phys. Ch. **37**, 168 (1901) and E. GOLDBERG Z. phys. Ch. **41**, 1 (1902).

²⁾ The first property is due to the activation occurring in the outer layer; from the sensitive substance only a limited number of molecules can be raised by the same quantity of light to the same degree of activity; even at a moderate dilution, the reaction becomes, on this account, independent of the concentration of the sensitive substance and therefore of the 0 order. This applies to slowly progressing reactions where the sensitive substance can be rapidly supplied by diffusion from the dark interior to the light zone.

ketone concentration (in regard to the sensitive substance a reaction of the 0 order).

By selecting the alcohol itself as a solvent the change in concentration thereof could be eliminated. (Table I).

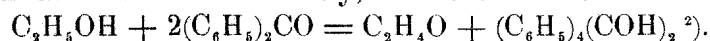
In order to determine the order of the reaction in regard to the alcohol, benzene was chosen as being a general, non-absorbing and non-reducing solvent. (Table Ia) (Chronologically these last experiments were made after the position of the active light in the spectrum had been ascertained; we, however, state them here because they enabled us to give a complete image of the course of the reaction.)

We notice that this reaction is indeed independent of the concentration of the ketone, but not independent, however, of the concentration of the alcohol. As the quantities thereof had been chosen in such a manner that they were amply sufficient even at the slightest concentration, it follows from the figures obtained that the velocity of the pinacone formation is proportional to the concentration of the alcohol.¹⁾

Thus we may represent the reaction by the kinetic equation:

$$\frac{d(\text{pinacone})}{dt} = K L. [\text{Alcoh.}]$$

With a constant light-quantity, the velocity of the pinacone formation thus becomes proportional to the alcohol concentration; how many molecules of the ketone act simultaneously cannot be ascertained in this manner. As, however, pinacone and aldehyde are formed and as according to the above equation one molecule of alcohol is attacked simultaneously, the reaction scheme becomes:



In order to learn the temperature coefficient the ordinary tubes (16 mm. diameter) were enclosed and sealed into a second tube (24 mm. internal diameter); the intervening space was filled with conductivity water and now two of these tubes were exposed to light as described, one of them being kept at 25°—28° and the other at 75°—78°³⁾.

¹⁾ Here we have assumed that the change in concentration of the alcohol during each of the four experiments was so slight that it could be regarded as being constant; this, of course, is not correct and we really ought to have taken each time a portion from larger apparatus. In that case, however, the experiments would become much more complicated, because the light-quantity did not then remain constant during the experiment. Hence, we have rested content with the above *modus operandi* which is sufficiently accurate for our purpose.

²⁾ For a mixture of ketone and benzhydrele we have proved this reaction scheme yet in another manner (see next communication).

³⁾ Compare R. LUTHER and F. WEIGERT, Z. phys. Ch. 53, 400 (1905).

TABLE I.

No.	Concentration of the ketone in 25 cc. alcohol	Quantity of pinacone	Remarks
1st Series			
1	0.1 gr. benzophenone	0.09 gr.	} entirely converted
2	0.25 " "	0.23 "	
3	0.50 " "	0.34 "	
4	0.75 " "	0.36 "	
5	1.— " "	0.36 "	
2nd Series			
1	1 gr. benzophenone	0.47 gr.	
2	2 " "	0.49 "	
3	3 " "	0.49 "	
3rd Series			
1	0.1 gr. o chlorobenzophenone	0.09 gr.	} entirely converted
2	0.25 " "	0.24 "	
3	0.50 " "	0.38 "	
4	0.75 " "	0.39 "	
5	1.— " "	0.39 "	
6	2.— " "	0.38 "	
7	3.— " "	0.39 "	
8	4.— " "	0.41 "	

TABLE Ia.

No.	Concentration of C_2H_5OH in the benzene solution of 2 gr. (C_6H_5) ₂ CO per 25 cc.	Quantity of pinacone	Ratio
1	0.2527 gr. or 1 eq.	0.08 gr.	1
2	0.5054 " " 2 "	0.18 "	2.25
3	1.0108 " " 4 "	0.36 "	4.50
4	2.0216 " " 8 "	0.66 "	8.25
5	∞ (pure alcohol)	0.69 "	

More accurate experiments were not considered necessary as we did not care for the absolute value, but only for the order of magnitude of the temperature coefficient.

Adjacent to the jacketed tube was also suspended an ordinary tube to ascertain whether the presence of the jacket had any influence on the pinacone formation.

The subjoined table II gives a survey of some series of experiments.

From these results it follows that the method is sufficiently accurate for our purpose, the ketone reduction is indeed a photo-reaction with a small temperature coefficient; this still falls below the mean stated by PLOTNIKOW¹⁾ of 1,17 per 10°.

TABLE II. Time of exposure 2—3 days.

No.	Contents of inner tube	t°	temp. interval	pinacone	$\frac{K_{t+10}}{K_t}$
1st Series					
1	2 gr. (C ₆ H ₅) ₂ CO in 25 cc. alcohol without jacket	25°—28°		0.45 gr.	
2 with jacket	"	} ± 50°	0.76 "	} 1.06
3	75°—78°		1.02 "	
2nd Series					
1 without jacket	25°—28°		0.44 gr.	
2 with jacket	"	} ± 50°	0.70 "	} 1.065
3	75°—78°		0.96 "	
3rd Series					
1	2 gr. (ClC ₆ H ₄) ₂ CO in 25 cc. alcohol without jacket	25°—28°		0.27 gr.	
2 with jacket	"	} ± 50°	0.35 "	} 1.095
3	75°—78°		0.55 "	
4th Series					
1 without jacket	25°—28°		0.24 gr.	
2 with jacket	"	} ± 50°	0.30 "	} 1.10
3	75°—78°		0.50 "	

¹⁾ Жон. ПЛОТНИКОВ. Photochemische Versuchstechnik. p. 273 (1912).

That the temperature coefficient for *ortho*chlorobenzophenone is really somewhat higher than for benzophenone seems to us rather probable, but this can only be ascertained by more delicate measurements¹⁾.

The independence of the concentration and the very small temperature coefficient now enables us to continue following this very simple method in the quantitative investigation as to the influence of the ketone to be reduced as well as of the reducing alcohol.

Influence of the alcohol.

The alcohols, as described above, were carefully dried over calcium and, after distillation, poured at once into the tubes containing two grams of ketone. These were then sealed and exposed to the light.

These tubes were suspended at such a distance that they could not interfere with each other.

The subjoined table gives two series of experiments, the first series was exposed for three and the second one for six days: particularly during the first days it was sunny spring weather.

What strikes us here in the first place is the agreement in the action of the alcohols 2—6; the secondary propyl alcohol gets oxidised somewhat more rapidly, the amyl alcohol a little more slowly. In the latter case a strong yellow coloration sets in.

Very much smaller is the velocity of the pinacone formation in the case of methyl and allyl alcohol; as no interfering yellow coloration occurred here and as the conditions were moreover quite equal, this different behaviour must be attributed to the particular position these alcohols occupy.

Although we cannot yet enter here into an explanation of the process, it is obvious that the reduction of benzophenone will proceed all the more readily when in the conversion of alcohol into aldehyde (or ketone) more energy is set free.

The absolute extent of this energy is unknown to us, but still some thermic *data* point to the existence of a parallelism in the

¹⁾ The remarkably greater reduction velocity in the jacketed as compared with that in an ordinary tube, must be attributed to the larger quantity of light which, owing to refraction in the jacket filled with water, falls on the inner tube. In fact nothing could be noticed of this inner tube when the tube was entirely filled; it looked as if the alcoholic solution has the width of the outer tube. In harmony with this observation, it appears that the ratios of the velocities in the four series namely 76:45, 70:44, 35:27 and 30:24 do not greatly diverge and are about equal to the proportions of the sections of the outer and inner tube 24:16. (Compare LUTHER and WEIGERT l. c. p. 391).

TABLE III.

N ^o . 1st Series	2 gr. benzophenone in 25 cc.	Quantity of pinacone	Remarks		
1	methyl alcohol	0.29 gr.	} faint yellow coloration strong yellow coloration		
2	ethyl alcohol	0.84 "			
3	<i>n</i> -propyl alcohol	0.85 "			
4	<i>sec.</i> propyl alcohol	0.95 "			
5	<i>n.</i> butyl alcohol	0.84 "			
6	amyl alcohol (Bp. 130 -133°)	0.75 "			
7	allyl alcohol	0.25 "			
2nd Series				Ratio 1' : 1'' etc.	
1'	methyl alcohol	0.49 gr.	} yellow coloration not much increased	1.69	
2'	ethyl alcohol	1.46 "			1.74
3'	<i>n.</i> propyl alcohol	1.49 "			1.75
4'	<i>sec.</i> propyl alcohol	1.60 "			1.58
6'	amyl alcohol (a. ab.)	1.05 "	} yellow coloration increased	1.40	
7'	allyl alcohol	0.42 "			1.68

velocity of the reduction and the extent of the difference of the molecular heat of combustion of alcohol and the correlated aldehyde (or ketone).

The greater this difference the more energy will be represented by the hydrogen atoms playing a rôle in that transformation.

As the heats of evaporation of the alcohols on one side and of the aldehydes on the other side do not sensibly differ and as all we require here are a few figures for comparison, a correction for this may be omitted here. We then find for these differences (according to *data* from the tables of LANDOLT-BÖRNSTEIN-ROTH). (See table IV.)

The heat of combustion of acetaldehyde is not known, neither that of formaldehyde. There is, however, a statement as to meta-formaldehyde: if from this one calculates the molecular combustion as if it were a monomeride, the difference amounts to 47 cal. As, however, this also includes the heat of polymerisation the difference is presumably considerably less than 47 calories.

TABLE IV.

Differences of the heats of combustion of:	methyl alcohol—(meta)formaldehyde	< 47.0 cal.
	ethyl alcohol—aldehyde	47.0 „
	<i>n.</i> propyl alcohol—propionaldehyde	50.0 „
	<i>sec.</i> propyl alcohol—acetone	51.0 „
	amyl alcohol (?)—valeraldehyde	47.0 „

The two series of experiments of table III were started at the same moment, the first was investigated after three and the latter after six days; when the converted quantity of substance is proportional to the quantity of light and no secondary hindrances occur, the proportion of the quantities of pinacone at each of the numbers 1 : 1', 2 : 2' etc. must be the same; these ratios have been inserted in the last column of the second series.

We notice that this ratio is indeed almost constant except in the case of amyl alcohol, where a hindrance in the form of an increasing yellow coloration is distinctly observed.

Influence of the ketone.

The tubes were filled with solutions of one gram of ketone in 50 cc. of absolute ethyl alcohol. Two series were exposed simultaneously to the action of the light; the first was investigated after three, the second after six days. Some pinacones remain very long in supersaturated solution, hence the alcohol was always distilled off and the residue shaken with 80 % alcohol so as to remove all unconverted ketone.

The subjoined table V gives the results obtained and the ratios of the velocities with those of the benzopinacone formation as unit.

Table VI gives a similar double series; most of the ketones investigated here were not attacked.

Table VII gives a survey of the results obtained in amyl alcohol as solvent and as reducing agent.

1st. The velocity of the pinacone formation, according to this survey, is greatly dependent on the nature and on the position of the substituent. As regards the nature, there is only one group (the methyl group on the two para-positions (N^o. 7)) that appears to accelerate the reduction velocity somewhat, for the rest the substitution causes a decrease in velocity.

This decrease is strongest when the substituting group is a phenyl

TABLE V.

No.	Name of the ketone	Quantities of pinacone				Ratio II/I	Ratio of the Re- duction-velocities with that of (C ₆ H ₅) ₂ CO as unit
		Series I	Series II	Series I	Series II		
		In grams		In millimols.			
1	benzophenone	0.41	0.85	1.12	2.32	2.05	1.—
2	2 chlorobenzophenone	0.12	0.25	0.28	0.58	2.07	0.25
3	3 chlorobenzophenone	?	±0.10	—	0.23	—	±0.1 (from II)
4	4 chlorobenzophenone	0.32	0.75	0.74	1.73	2.34	0.66
5	4 methoxybenzophenone	0.39	0.80	0.92	1.88	2.04	0.82
6	4 methylbenzophenone	0.41	0.86	1.04	2.18	2.09	0.93
7	4,4' dimethylbenzophenone	0.48	0.95(off)	1.19	—	—	1.06
8	4 bromobenzophenone	0.51	0.98(off)	1.—	—	—	0.90
9)	4,4' dichlorobenzophenone	?	0.73	—	1.45	—	0.63 (from II)
10	2,2',4,4' tetrachlorobenzoph.	0.22	0.47	0.34	0.72	2.12	0.30
11	2 chloro 4' methyl „	0.27	0.55	0.58	1.18	2.03	0.52
12)	4 chloro 4' methyl „	0.19	0.70	0.41(?)	1.50	3.66(?)	0.64 (from II)

TABLE VI.

13	benzophenone	0.85	0.98(off)	2.35	—	—	1
14)	4 phenylbenzophenone	—	—	—	—	—	0
15	phenyl- α -naphthylketone	—	—	—	—	—	0
16	phenyl- β - „	—	—	—	—	—	0
17	2 methylbenzophenone	—	—	—	—	—	0
18	3 methylbenzophenone	0.80	0.96(off)	2.03	—	—	0.89
19	2,4,2',4' tetramethyl „	—	—	—	—	—	0
20	fluorenone	—	—	—	—	—	0

TABLE VII. Amyl alcohol as solvent.

21	benzophenone	0.75	0.97(off)	2.05	—	—	1
22	2 chlorobenzophenone	0.22	0.33	0.51	0.76	1.49	0.25
23	4 chlorobenzophenone	0.65	0.96	1.49	2.20	1.48	0.72
24	4 methylbenzophenone	0.74	0.96(off)	1.88	—	—	0.91
25	phenyl α -naphthylketone	—	—	—	—	—	0

1) These ketones had not entirely passed in solution in the alcohol.

group, because 4-phenylbenzophenone (14) and the two phenyl-naphthylketones (15 and 16) are not reduced.

Halogen atoms and methyl groups *do* diminish the single substitution, but (with one exception) do not prevent the same. Para substitution has the least influence, ortho the greatest; this, however does not apply to the chlorobenzophenones (3), so that we can hardly speak of a universal rule.

The symmetry of the molecule seems to accelerate the velocity.

Whereas the 4-methylbenzophenone has a smaller velocity than the benzophenone (5), the 4,4'-dimethylbenzophenone has a somewhat greater one. The fairly considerable decrease in velocity in the 4-chlorobenzophenone (4) is not continued in the 4,4'-dichlorobenzophenone (9). In connexion with the considerable decrease in the 2-chlorobenzophenone (2) that in the 2,2',4,4'-tetrachlorobenzophenone (10) is unexpectedly high.

A remarkable fact is the slight influence of the methyl group on the meta position (18) in regard to the great one of the chlorine atom (3).

2nd. Of more importance is the fact that the alcohol, the reducing agent, is of very secondary significance as regards the ratio of the reduction velocities; this is shown from the comparison of tables V and VII. The ratio of the velocities in ethyl and amyl alcohol is practically the same. We have completed these observations with a few on methyl and propyl alcohol, selecting methyl alcohol because the velocities therein are generally much less, whereas o-chlorobenzophenone with benzophenone were compared as ketones, because the velocities in ethyl (and amyl) alcohol differ strongly.

The subjoined table VIII gives a survey of the results.

TABLE VIII.

	Sol. C ₂ H ₅ OH, 1 st Series		Sol. C ₃ H ₇ OH, 3 rd Series		Sol. CH ₄ OH, 4 th Series		Sol. nC ₃ H ₇ OH, 5 th Series	
	Quantity in m.mols.	Ratio	Quantity in m.mols.	Ratio	Quantity in m.mols.	Ratio	Quantity in m.mols.	Ratio
Benzophenone	2.32	1.0	2.05	1	1.91	1	2.93	1
2 Chloro „	0.58	0.25	0.51	0.25	0.46	0.24	1.08	0.27
4 „ „	1.73	0.66	1.49	0.72				
4 methyl „	2.18	0.93	1.88	0.91				
phenyl α-naph- thyl ketone } }	0	0	0	0				

First of all it follows from this constant ratio that the *ketone* is prominent in the photo-reaction, that this passes into a photo-active condition. Further, that the diverse ketones are activated in a perfectly analogous manner in such a way that either a number of molecules (the same for all ketones) become photo-active, which molecules then react with the alcohol with a velocity specific for the ketone; or, a number of molecules specific for each ketone becomes activated which, with a definite velocity which is independent of the ketone, dehydrogenises the alcohol.

A choice from these alternatives can only be made by a further study of the photo-reaction.

The active light of the ketone reduction.

The first attempt to ascertain the position of the active light in the spectrum has been made by CIAMICIAN and SILBER¹⁾. They investigated, for instance, the reduction of benzophenone and alcohol, employing two photo-filters.

As a red photo-filter was used a cold saturated solution of fluorescein in alcohol (thickness of layer 15 mm.) which extinguishes all light to 0.510μ ; by adding gentian-violet the absorption could be raised to 0.620μ .

As a blue filter served a 10% solution of cobalt chloride in alcohol which transmits rays of a wavelength less than 0.480μ ; a green band at $\pm 0.560 \mu$ and a red one at $\pm 770 \mu$ remain, however, unextinguished. They arrive at the result that all the reactions with which they were engaged, took place under the influence of *blue* light. We have used a larger number of photo-filters and carried out the research in jacketed tubes; the inner tubes were those which were used by us in the other experiments; the intervening space was 15 mm. Above the liquid in the jacket the outer tubes were covered with black lacquer, so that none but filtered light could penetrate into the inner tube.

As photo-filters were selected:

- I. Red: aqueous solution of chrysoïdin²⁾.
- II. Green: „ „ „ potassium dichromate + acid green B. extra.²⁾

Blue and violet.

- III. 10% alcoholic solution of CoCl_2 .
- IV. Cold saturated aqueous solution of crystal violet 5 B. O.²⁾.
- V. „ „ „ „ „ acid violet 4 B. N.²⁾.
- VI. Solution of iodine in CCl_4 .

¹⁾ B. 35, 3593 (1902)

²⁾ Colouring matters from the "Gesellschaft f. chem. Ind. Basel".

In agreement with that found by CIAMICIAN and SILBER for the red fluorescein filter we found that the filters I and II which only transmit red (690—598 $\mu\mu$) or red and green ($> 500 \mu\mu$) absorbed all actinic rays.

Also V, which besides red rays of about 700 $\mu\mu$ still transmitted blue and violet $> 433 \mu\mu$, completely prevented the reduction in the inner tube. On the other hand an important reduction took place with the filters III, IV, and VI which transmitted rays to the extreme, visible violet $\pm 400 \mu\mu$.

The series of experiments were conducted in this way that a set of four jacketed tubes with photo-filters were exposed to sun-light for some days in front of the white screen: the results are contained in the subjoined table.

TABLE IX.

N ^o .	Ketone in the inner tube	Photo-filter	Quantity of pinacone in gr.	Remarks
1st Series				
1	2 gr. benzophenone in 25 cc. C ₂ H ₅ OH	I	0	entirely converted
2	II	0	
3	III	2	
4	IV	0.67	
2nd Series				
5	III	0.85	From the comparison of the figures for III and IV with the controlling tube with conductivity water it appears that there always takes place a partial absorption of the actinic rays; this, however, is relatively small and is probably based on a general absorption, which in a spectroscopic investigation was readily observed.
6	V	0	
7	VI	0.48	
8	{ conductivity water	1.28	
3rd Series				
9	2 gr. o-chlorobenzophenone . .	III	0.33	From the comparison of the figures for III and IV with the controlling tube with conductivity water it appears that there always takes place a partial absorption of the actinic rays; this, however, is relatively small and is probably based on a general absorption, which in a spectroscopic investigation was readily observed.
10	V	0	
11	VI	0.28	
12	{ conductivity water	0.42	

Now with this method we can only get a very rough determination of the position of the active region, still it appears that the active rays are presumably situated in the violet and have a wavelength smaller than $\pm 430 \mu\mu$. In order to see whether in the beginning of the ultraviolet active rays were still present, a small jacketed tube was constructed from quartz, the alcoholic benzophenone solution was put into the inner tube and in the jacket a cold saturated solution of 'nitrosodimethylaniline'¹⁾ which absorbs all visible violet and blue rays and transmits ultra-violet ones of 400—280 $\mu\mu$.

Neither in sun-light, nor in front of the quartz lamp did any reduction set in; from this we could conclude that the active rays were not situated in the ultra violet, but in the visible spectrum < 430 and $> 400 \mu\mu$.

A fortunate incident now came to our aid when we were engaged in determining the correct position of the active light.

We had noticed that the ketones were converted with comparatively great rapidity into pinacones by means of the HERÄUS quartz-mercury lamp.

The mercury spectrum must thus contain a great quantity of the chemically active rays. This spectrum exhibits a very intensive blue line at 436—434 $\mu\mu$ and two violet ones at 407,8 $\mu\mu$ and 404.7 $\mu\mu$ ²⁾.

Photo-filter V completely removes the violet lines and leaves the blue ones unchanged; as this filter in sunlight as well as in front of the quartz lamp prevents all conversion of benzophenone as well as of *o*-chlorobenzophenone, and as we have noticed that the ultra-violet light of the lamp is inactive we may conclude that the active light for the photochemical reduction of the aromatic ketones is situated in the extreme end of the visible violet.

The fact that the nature of the source of light has no principal influence on the reduction process is shown from the subjoined table, in which are given the ratios of the quantities of pinacone that are formed from diverse ketones when exposed either to sun-light or mercury-light.

The exposure to mercury-light was carried out by placing a solution of 0.5 gram of ketone in 15 cc of ethyl alcohol at a distance of 5 cm from and parallel to the quartz lamp and exposing these for 10 hours; hence, the quantity of light was approximately the same for all ketones.

The close agreement of these ratios also renders it probable that

¹⁾ Compare PLOTNIKOW etc. p. 19.

²⁾ LEHMANN, Phys. Zeitschr. 11, 1039 (1910).

TABLE X.

No.	Name of the ketone	Quantity of pinacone on exposure to Hg light		Quantity of pinacone on exposure to sunlight with benz. pinacone as unit
		in grams	in m.mols. with benzopinacone as unit	
1	benzophenone	0.35	1	1
2	2 chlorobenzophenone	0.10	0.23	0.25
3	4 chlorobenzophenone	0.30	0.70	0.66
4	2 methylbenzophenone	0	0	0
5	4 methylbenzophenone	0.34	0.89	0.93
6	phenyl α -naphthylketone	0	0	0
7	fluorenone	0	0	0

the active rays are situated for the greater part at 407.8 and 404.7 μ ¹⁾.

The action of light on mixtures of ketones.

The phenomena observed by us during the exposure to light of ketone mixtures in absolute alcohol divulged a very strong mutual influence.

In order to better understand these observations, the following should precede:

We have noticed that the chemically active light comprises a very limited part of the spectrum, yet, therein are rays of different frequency and intensity.

A. We can now suppose that each of the ketones present wants its own active rays without absorbing rays intended for the other ketone; then — as the pinacone formation is independent of the concentration — there will have formed in the tube with the mixture the sum of the quantities of pinacone that are formed in the separate tubes under the same conditions.

Those quantities within certain limits must also be independent of the proportion of the concentrations of the ketones in the tube containing the mixture.

1) Presumably, the action is in a high degree selective, as a layer of 3 mm 4% benzophenone in absolute alcohol certainly caused a very distinct fading of these two mercury lines, whereas nothing could be noticed of a curtailing or fading at the violet side of the arc lamp spectrum through that same liquid layer. We attach, moreover, not much value to this subjective observation, for only an accurate spectrophotometric investigation of the absorption spectra of the ketones can properly determine the connexion between absorption and chemical action.

B. As soon, however, as rays for the one ketone are also consumed by the other one, the quantity of pinacone will be less than the sum in question and, moreover, the proportions of concentrations will no longer be a matter of indifference.

For in the layer where the photo-reaction takes place each molecule of the one ketone requires a part of the light-energy also wanted by the second ketone, so that the hindrance experienced by the latter will become greater when its relative concentration gets less.

C. The extreme case would be that both ketones require just the same rays; we should then obtain a quantity of each of the ketones which in equimolecular concentration is equal to half the quantity that forms in the tube with the separate ketone (always supposing that no other obstacles occur).

The phenomena recorded by us are now best understood from the supposition B: a ketone does require specific rays from its neighbour. Some of the observations approach to A, others to C, some even exceed this extreme case, showing that the action is more complicated than was at first supposed, as will appear from the subjoined tabulated survey.

TABLE XI.

1st Series No.	Solution of 2 gr. of <i>o</i> -chlorobenzophenone and varying quantities of phenyl α -naphthylketone	in 50 cc. alcohol	Quantity pinacone in gr.	Remarks
1	2 gr. <i>o</i> -Cl benzophenone pure		0.84	For one of the ketones of the mixture was selected a substance that did not form pinacone. The case thus became a peculiar one but simple of execution.
2	" +0.1 gr. phenyl α -naphthylketone		0.30	
3	" +0.25 " " "		0.12	
4	" +0.50 " " "		0	
5	" +1.— " " "		0	
2nd Series No.	As above <i>o</i> -Cl benzophenone and varying quantities of <i>o</i> -methylbenzophenone		Quantity pinacone	Remarks
1	2 gr. <i>o</i> -Cl benzophenone pure		0.37	As above
2	" + 0.1 gr. <i>o</i> -CH ₃ benzophenone		0.36	
2	" + 0.25 " "		0.30	
4	" + 0.50 " "		0.26	
5	" + 1.— " "		0.15	

We notice that when one of the ketones does not get reduced it exerts a very powerful retarding action on the reduction of the other ketone.

This action, particularly with phenyl- α -naphthylketone is much more important than we should expect even in the extreme case C; besides the elimination of the chemically active rays, the molecules of the naphthylketone must cause an impediment, which may, perhaps be put on a par with the obstruction caused by oxygen in the photo-halogenations.

TABLE XII.

No.	Solutions of various ketones, which are reduced separately in 50 cc. solution.	Quantity of pinacone formed.	Quantity of calculated mixture pinacone	Halogen content found %.	Halogen content calculated.	Remark
1st Series						The figures given in column 4 and 6 are calculated from the supposition A (v. p.) that the ketones do not exert an impeding action on each other. As to the ratios employed compare Table V (p. 859).
1	2 gr. benzophenone	1.71	1.71	—	—	
2	2 » » + 2 gr. o-Cl benzophenone	2.31	2.37	4.16	3.8	
3	2 » » + 1 » »	2.18		3.46		
2nd Series						
1	2 gr. benzophenone	1.66	1.66	—	—	
2	2 » » + 2 gr. p Cl benzophenone	2.18	2.76	9.19	7.2	
3	2 » » + 1 » »	1.69		3.19		
3rd Series						
1	2 gr. benzophenone	0.85	0.85	—	—	
2	2 » » + 2 gr. p Br benzophenone	1.65	1.95	23.9	19.0	
3	2 » » + 1 » »	1.05		11.4		

From Table XII it appears that, in the case when both ketones are reduced, we have demonstrated a considerably less impediment than in the case that one of them is not reduced. Still, there is always a negative influence, we obtain in all cases a quantity less than the sum of the quantities which we should have obtained in separate tubes; we are always dealing with case B.

In this we notice the smallest mutual hindrance in the mixture of benzophenone and o-chlorobenzophenone, yet we notice plainly that the impediment increases when one of the ketones is present

in large excess (1st series N^o. 3) and that in such a case that present in the smallest amount is the most strongly impeded. Much more pronounced is the hindrance observed with mixtures of benzophenone and p. Cl- or p. Br-benzophenone; the sum of the pinacones remains here far below the calculated quantity. The halogen ketone has as a rule a stronger impeding action than benzophenone, for even in smaller quantities than the molecular ones (N^o. 2 of the three series) the halogen pinacone in the mixture is predominant. Only with a considerable excess of benzophenone the halogen pinacone is repelled and mostly so in the cases where the greatest hindrance is present (compare N^o. 3 of the three series).

We thus find in rough traits what we could expect; there occur, however, particularly when one of the ketones is not reduced separately, such great hindrances that they cannot be satisfactorily

TABLE XIII.

N ^o .	Contents inner tube 2 gr. benzophenone in 20 cc. abs. alcohol	Contents outer tube 50 cc. abs. alcoholic solution of 4 grams:	Quantity pinacone		Quantity of pinacone in the inner tube with the blank tube as unit.
			inner tube	jacket	
1 st Series		alcohol (blank-exper.)	0.64	—	1.—
	2	p CH ₃ benzophenone	0.28	0.66	0.44
	3	o Cl benzophenone	0.18	0.19	0.28
	4	phenyl- α -naphthylketone	trace	0	trace
2 nd Series		alcohol (blank-exper.)	1.05	—	1.—
	2	o CH ₃ benzophenone	0.50	0	0.48
	3	phenyl- β -naphthylketone	0.28	0	0.27
	4	fluorenone	0	0	0
3 rd Series		alcohol (blank-exper.)	0.79	—	1.—
	2	p Br benzophenone	0.42	1.18	0.54
	3	p Cl benzophenone	0.38	0.83	0.47
	4	benzophenone	0.29	0.93	0.37

explained in the above cited manner. There seems to be a connexion here between the extent of the impediment and the non-appearance of the photo-reduction.

Now, in order to eliminate the hindrance which might eventually take place owing to the mixing, the oft-quoted jacketed tubes were filled in such a manner that in the inner tube was always inserted a definite ketone and in the jacket diverse other ketones.

The light then first traversed a ± 2 mm. thick layer of a ketone then to exert its action on the benzophenone; in this way we could form a better opinion as to the absorption of rays of light by the one ketone (in the jacket) which were needed for the other ketone (in the inner tube).

There exists no doubt that *all* ketones absorb actinic rays intended for the benzophenone; the degree of this absorption is certainly very different and specific.

The ketones which were attacked in the jacket were, during the experiment, reduced in concentration, so that the conditions for the reducing of the benzophenone in the inner tube gradually became more favourable; this causes, however, that we can only consider as fairly comparable the experiments where no reduction takes place in the jacket. Hence, a few ketones have been placed in the jacket in benzene solution whilst in the inner tube was again present a solution of 2 grams of benzophenone in 20 cc. of absolute alcohol; the following result was thus obtained:

TABLE XV.

N ^o .	In the inner tube 2 gr. (C ₆ H ₅) ₂ CO in 20 cc. abs. alc.	In the jacket a N/4 benzene solu- tion of	Quantity of pinacone in the inner tube.		Remarks
1		— (blank)	1.34	1.0	The benzene solution in the jacket was al- ways coloured pale yellow which colour again faded in the dark.
2		benzophenone	0.45	0.34	
3		o-chloro >	0.53	0.40	
4		p- > >	0.34	0.25	
5		p-methyl >	0.40	0.30	

It appears that several ketones absorb rays of light which effect the benzophenone activation, even when they are dissolved in benzene.

The reversible yellow coloration of this benzene solution, however, tells us to be careful, for the activated ketone can form with benzene

a light-screen, thus causing the absorption effect to be greater than when the ketone had been present in alcoholic solution.

In each case a circumstance occurs owing to which the phenomenon becomes more complicated, so that from these last experiments we may at most draw the conclusion that rays of light are indeed always absorbed by the one ketone, which the other required for the oxidation of alcohols.

The most powerful absorbing ketones appear mostly — but not always — to oxidise the alcohol slowly or not at all, so that we gain the impression that a liberal absorption does take place, but that the possibility of the setting in of a reaction and its velocity does not only depend on the alcohol, but in a great measure on the ketone.

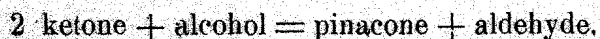
It speaks for itself that the experiments on this almost quite unexplored region can only bear a very provisional character; still we believe we have attained, with very simple means and methods, some results which will prove of importance for the insight into the photochemical reactions.

For the moment, however, we wish to refrain from an attempt to explain the phenomena observed until more accurate spectrophotometric *data* are at our disposal.

S U M M A R Y.

- I From aromatic ketones and alcohol are formed, in the light, exclusively pinacones; these latter are, therefore, the products to be first isolated in the reduction. Hydrols are, in the reduction of the aromatic ketones, always formed secondarily (see Proc. XVI 91 and 962) either from the pinacones or from the primarily formed half pinacone molecules.
- II 1. The photo-reduction of the ketone by alcohols was studied by exposing simultaneously to the light a set of tubes of equal dimensions and filled with equal quantities of liquid, thus causing the light-quantity (i. t) for each object of a serial experiment to be equal.
2. The velocity of the pinacone formation appeared to be independent of the concentration of the benzophenone and proportional to the concentration of the alcohol. Hence, it satisfied the equation:

$$\frac{d \text{pinacone}}{dt} = KL \cdot [\text{alcohol}] \text{ and, therefore, the reaction scheme:}$$



3. The temperature coefficient was small: 1.06—1.11 for 10°.
4. The velocity of the pinacone formation is greatly dependent on the alcohol; for instance, the methyl alcohol and the allyl alcohol were oxidised much more slowly than other primary and secondary alcohols.
5. The velocity of the pinacone formation is greatly dependent on the ketone, the benzophenone is attacked rapidly, most of the ketones as yet examined less rapidly, many not at all.
6. The ratio of these velocities in different alcohols is constant.
7. The active light of the ketone reduction is sure to be situated in the spectrum between 400 and 430 $\mu\mu$ and very probably in, or adjacent to, the rays 404.7 and 407.8 of the mercury quartz lamp.
8. The ratio of the velocities of the pinacone formation in sunlight and in mercury light is the same.
9. When two ketones are present simultaneously one of them absorbs a part of the rays required by the other ketone; this also appears when the light passes through a solution of the one ketone and falls on that of the other.

Particularly in the case of the powerfully absorbing ketones the hindrances are stronger than was to be expected.

Delft, October 1914.

Physics. — “*Simplified deduction of the formula from the theory of combinations which PLANCK uses as the basis of his radiation-theory.*” By Prof. P. EHRENFEST and Prof. H. KAMERLINGH ONNES.

(Communicated in the meeting of Oct. 31, 1914).

We refer to the expression

$$C_P^N = \frac{(N-1+P)!}{P!(N-1)!} \dots \dots \dots (A)$$

which gives the number of ways in which N monochromatic resonators R_1, R_2, \dots, R_N may be distributed over the various degrees of energy, determined by the series of multiples $0, \epsilon, 2\epsilon \dots$ of the unit energy ϵ , when the resonators together must each time contain the given multiple $P\epsilon$. Two methods of distribution will be called identical, and only then, when the first resonator in the one distribution is at the same grade of energy as the same resonator in the second and similarly the second, third, \dots and the N th resonator are each at the same energy-grades in the two distributions.

Taking a special example, we shall introduce a symbol for the distribution. Let $N = 4$, and $P = 7$. One of the possible distributions