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

Chemistry. — *"Observations about hydration under the influence of Colloidal Catalysers and how to account for this process"*. By Prof. J. Böeseken and Mr. H. W Hofstede.

(Communicated in the meeting of June 30, 1917).

Some time ago [1]) we performed and described a number of hydrations with the aid of colloidal catalysers. At the same time we gave an outline of what might be expected during the development of this process, and what we shall therefore observe in measuring the absorption of the hydrogen, viz:

The hydrogen and the matter to be reduced will pass from the gas-space into the liquid medium, then they will pass one or more layers covering the atoms of the catalyser and finally they will coalesce. Hence we first observe a succession of diffusion-processes, before the catalytic-chemical reaction enters. It was assumed that the rapidity of the latter process is always considerably greater than that of the former, so that the observed rapidity of absorption, would seem to refer to a diffusion-process.

The assumption of the all-surpassing velocity of the catalytic-chemical process is arbitrary; the rapidity will of course depend on the nature of the catalyser. But we have been guided in the first place by the consideration that the action of platina-metals on some of the processes brought about by them is exceedingly great indeed, so that few thousandths millimol are sufficient to bring molecular quantities to a fairly rapid chemical change.

It appears then that we want far greater quantities of catalyser, say from 50—100 millimol, to reach the result, obtained in the observations made. So it is obvious that we must rather look for the cause of that very moderate velocity in the possibility, that of these 50—100 millimol only a very small part can be reached at the same time by the reacting substances, than to suppose that the process of *these particular* reactions is such an extraordinarily slow one.

In my opinion the very potent catalytic action of the metal-atoms results from the nature of these atoms themselves. Owing to their

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[1]) Recueil **35** 260 (1916).

demonstrated that the analytic-chemical reactions proper have certainly not been measured by us.

1. The velocity of reduction of α-crotonic acid, isocrotonic acid and tetrolic acid under the influence of a very active palladium-catalyser (PAAL [1])) was perfectly equal under otherwise equal conditions.

2. The reduction and substitution of trichloroacrylic acid to propionic acid and the substitution of pentachloropropionic acid took place without any sudden changes of velocity and even for these two acids with almost equal velocity.

3. The two double bonds of the sorbinic acid were hydrated without any sudden change of velocity, and the velocity was equal to the substitution-velocity of the two chlorated acids mentioned under 2.

4. It was ascertained (with a less active catalyser) that cinnamic acid, muconic acid, malonic acid and vinylglycolic acid were hydrated almost quite as rapidly, if only the decreasing activity of this catalyser was taken into account.

5. The result obtained with a relatively large quantity of palladiumsol (SKITA [2])) that under otherwise equal conditions, equimolecular quantities of cinnamic acid, glutaconic acid, muconic acid and vinylglycolic acid were hydrated with approximately equal velocities whereas itaconic acid, mesaconic acid and citraconic acid were hydrated, with somewhat lesser velocities, though mutually equal ones, than the former acids.

6. It is true that during the reduction of the cinnamic acid under the influence of finely divided platinum, a decrease of velocity was noticed after the absorption of about one molecule of hydrogen; it could be determined however, that this divergence decreased in proportion as a greater quantity of the catalyser was taken. This cannot be accounted for if we assume a chemical cause of the decrease in velocity, which is besides very slight and not very perceptible.

7. It was found that the velocity of the hydration was largely dependent on the condition of the catalyser p. 275—279 and p. 286.

8. The temperature-coefficient was but a small one (We do not set great store by this argument, because an increase of temperature may cause a diminution of the surface of the catalyser, the result of which will be a decrease of velocity).

[1]) B. 38, 1401 (1905).
[2]) B. 37, 24 (1904), 40. 2209 (1907), 41. 805 (1908).

§ 2. Now the very rapid hydration of undecylenic acid-sodium, with palladium-sol, during which process the contents of the reaction-vessel were changed into a froth (p. 270), had revealed to us that the method of investigating pursued up till now, did not sufficiently guarantee the demand that' we should keep the paralysis-layers about the catalyser saturated with H_2.

Hence it was necessary :

1. to improve the hydration-vessel ;

2. to take a quite definite catalyser, if possible the activity of the same must be constant, and at any rate easy to control ;

3. to work in a constant temperature.

As regards the first requisite we selected the apparatus employed by Mr. COHEN and one of us in our experiments on light, with which the H_2 is spouted in small particles with great velocity through the liquid [1]), the contact-surface of the gas with the colloidal catalyser being thus very considerably enlarged. This is brought about by rotating a hollow stirrer with great rapidity through the liquid ; in the gas-space above the surface of the liquid is an opening. During the rotation the gas is sucked through the stirrer and dashed into small bubbles against a wave-breaker. This wave-breaker keeps the fluid-level constant.

A revolution-counter indicated that the number of revolutions was at least 2200 a minute. It is probable that we succeeded in keeping the paralysis-layers saturated with hydrogen, as with a much slighter velocity of rotation the same velocity of hydration was obtained in otherwise similar conditions and when applying but moderate quantities of the catalyser.

As catalyser we used the palladiumsol prepared according to SKITA and MEYER [2]), which proved to be very active, so that we needed but few milligrams of metal to obtain a velocity of hydration that could be measured. The hydration-apparatus was placed in a thermostat, in which was also an electric lamp, so that the vessel could be observed without taking it out of the thermostat. We were enabled to do so, because the hydration-apparatus had been fixed in an iron frame-work that could be moved up and down with the apparatus.

The hydrogen was purified by conducting it through alkaline and acid permanganate of potassium, through silver nitrate, through alkaline pyrogallol solution and finally through concentrated sulphuric acid.

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[1]) Proc. Kon. Ak. Wet. 25 March 1916.

[2]) B. **45**, 3579 (1912); one c.c.m. contained one m.g. of palladium.

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Before use the palladiumsol had been saturated with hydrogen, the gas was also conducted for some time through the hydration-vessel, while the spray-stirrer had been brought into action, and the substance to be reduced was already in the vessel.

By means of a three-way tap the hydration-vessel was connected with a graduated Lunge-burette, which the H_2 filled. By means of a simple lever-apparatus gas-volumes could always be read during a constant mercury-level. The accompanying figures show the complete installation in elevation and in plan. By way of elucidation it may be remarked that in the drawing we find between the purification-flasks of the hydrogen and the dryingflasks a copper tube with iron mantle, filled with copper-shavings. This tube is heated in a chamotte-oven and serves to free the hydrogen from oxygen. The ends of this metal tube are provided with refrigeration-jackets. (See below).

The first experiments were made with cinnamic acid in aqueous solution at high temperature and without thermostat; afterwards in 96 % alcohol at the usual temperature. Herein the catalyser frequently proved to flock out, so that we finally worked in 80 % alcohol, always about 25°. Besides cinnamic acid, we also examined other substances.

With the readings of the hydrogen that had been absorbed we noticed the barometer and the temperature in the neighbourhood of the gas-burette; as a rule we took 3 m.g. palladiumsol against 0.5 to 1.5 gr. of the hydrated substances.

We subjoin a tabulated summary of a series of experiments.

The summary gives two series of experiments; in the first series of 15 the H_2 had not been conducted along a red-hot copper-spiral.

Though the character of the results obtained is in accordance with what was found before, yet it appears even in a superficial investigation that great irregularities occurred.

The velocities of hydration diverged in a rather considerable degree under comparable conditions; this is especially striking in the reduction of the cinnamic acid-aethylesters where the initial-velocity of absorption was found to be within the limits 5.5 and 80 c.m. per 10' (N°. 8—11).

The cinnamic acid-methylester too revealed strange leaps, the commencing velocity being between 10 and 40 ccm. per 10'.

Then we were struck with another phenomenon, viz. that not unfrequently the number of absorbed cc.m. H_2 surpassed the number calculated to a considerable extent; we had observed this before and this fact has been repeatedly observed by other investigators

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No.	Substance	Quant. in gr.	Solvent	Quant. in ccm.	Pd-sol. in ccm.	ccm H_2 calculated	ccm H_2 absorbed	Velocity in ccm. per 10'	T.	Observations
1	Cinnamic acid	0.7265	H_2O	75	3	117	118	25	94°	Irregular
2	"	0 4792	"	"	"	62	78	"	"	Idem.
3	"		96 % alc.	"	"	146	144	13	18	Very regular
4	Undecylenic acid-aethylester	1.3010	"	100	"	147	149	80	18	After the first 10' a considerable retardation; flocking-out.
5	"	1.6514	"	"	"	189	192	110	16	Idem.
6	"	1.1263	80 % alc.	"	"	132	130	92	17.7	Retardation; no flocking-out.
7	"	1.2387	"	"	5	144	143	105	18.2	Idem
8	Cinnamic acid-aethylester	0 8909	"	75	3		113	5.5	26	The course of the hydration was a very slow one, cause: very pure H_2(c.f.text).
9	"	1.0971	"	"	"	175	153	75	"	Hydrogen contained O_2; course very regular.
10	"	0 9533	"	"	"	155	133	80	"	Idem.
11	"	1.3059	"	"	"			28	"	Course auto-catalytic, was not continued up to the end.
12	Cinnamic acid-methylester	0.6840	"	100	"	158	103	40	"	Hydrogen contained O_2.
13	"	0.8447	"	"	"			± 10	"	Great retardation, cause unknown.
14	"	3.0390	"	"	"	493	447	35	25	Hydrogen contained O_2
15	"	2.1397	"	"	"	351	313	40	"	Idem.
16	"	8.0519	"	"	"	1276	1161	± 50	"	Idem; course auto-catalytic.
17	"	2.0832	"	"	"	"	"	1	"	H_2 very carefully purified, from oxygen.
18	"	not meas	"	"	"	"	"	58	"	H_2 not conducted over Cu-spirals.
19	"	"	"	"	"	"	"	56	"	Cu-spiral was used, but H_2 still contained O_2; very regular reduction.
20	"	2.1102	"	100	"	314	308	52	"	Strongly inclined curve
21	"	2.0403	"	"	"	303	299	45	"	Idem.
22	"	2.0176	"	"	"	295	294	"	"	Idem; towards the end almost completely paralysed.
23	Cinnamic acid-aethylester	1.4190	"	"	2 after 30' still 3	193	189	8 after 30' 100	"	Partially flocked-out, after the addition of 3 ccm Pd. sol unexpectedly strong acceleration, then paralysis again.
24	"	2.0210	"	"	1 after 30' still 1 etc. (c.f. text)	283	270	(c.f. text)	"	
25	"	2.3121	"	"	1 after 30' still 1 etc.			"		No flocking-out; but decrease of velocity.
26	"	2.2081	"	"	dito	313	288	"	"	Idem.

as well. In our first experiments we had used the hydrogen out of a KIPP apparatus and had conducted it through a flask with alkaline pyrogallol-solution; the quantities of hydrogen that had been calculated and measured did not diverge greatly.

Afterwards we employed a hydrogen-bomb and obtained far too great absorption-numbers (nos. 9, 10, 12, 14 and 15). At first not being prepared for the presence of oxygen in the purified gas we excluded as well as we could all other sources of the coming in of oxygen in the apparatus by repeated washing, preliminary treatment of the palladium, and the avoiding of rubber-junctions.

When however the surplus continued, the presence of oxygen was thought probable and determined in the following way.

1). By hydration of larger quantities of substance in the same quantity of solvent and with the same amount of catalyser.

And indeed it was found that on applying:

$\pm$ 1 gram cinnamic acid-methylester the surplus $=$ 55 cc.m. N°. 12.

3 ,,   ,,   ,,   ,,   ,, $= 46$,, ,, 14.

8 ,,   ,,   ,,   ,,   ,, $= 115$,, ,, 16.

In case of the presence of oxygen in the hydrogen the surplus used must be approximately proportional to the quantity of methylester reduced, if at least the amount of the oxygen in the H_2 is constant. Whereas we conducted the gas through an alkaline pyrogallol solution, this will surely not have been the case, but an increase of the surplus when applying more substance is indubitable.

2). By some blank experiments.

For this we took 100 ccm. 80 % alcohol and 3 ccm. palladiumsol saturated with H_2, they were put into the hydration-vessel, after it had been filled with hydrogen in the usual manner.

We actually observed an absorption of gas in four control-experiments, it amounted to between 20 to 30 ccm.; it is curious that though far more gas was in the burette, the action came to an end with this.

The cause of it may be, that on account of diffusion all oxygen had come from the burette into the hydration-vessel, or that the catalyser is paralysed; the former cause seems the more probable. Now the hydrogen was freed from oxygen by means of a tube with red-hot copper shavings; hereupon a decrease of only one ccm. took place in 60'.

But when we were now going to hydrate the cinnamic acid-methylester with this very purified hydrogen, which had also been carefully freed from oxygen, the process was an extremely slow one. (N°. 17).

Of course this might be due to an accidental paralysis of the

catalyser; in order to investigate this the Cu-spiral was switched off without substituting a pyrogallöl-solution, the reduction was once more very regular and even took place with greater velocity than when the pyrogallol-solution was used. (N°. 19).

The Cu-spiral was switched on again, but this time it had evidently not completely freed the hydrogen from oxygen, as the course of the reaction was fairly rapid and regular. (N°. 19).

Therefore some quantitative experiments were started with the Cu-spiral as above; the reaction took place; but no paralysis set in, it appeared finally that 6 ccm. too much had been absorbed. As the contents of the hydration-vessel are ± 600 ccm., and 300 ccm. have been received from the burette, the total amount of gas that has been in contact with the catalyser amounts to ± 900 ccm. The surplus 6 ccm. corresponds to 2 ccm. O_2, hence its amount is ± 0.2 %. So this quantity proves to be amply sufficient, to keep up the reaction. (N°. 20).

With a subsequent experiment (N°. 21) we had reduced the O_2-quantity (calculated from the surplus gas that had been used) to 0,1 %; otherwise everything being similar; the velocity of reduction was appreciably less and a stronger retardation set in.

This was still more obvious, when we had decreased the O_2-quantity to 0,003 %; towards the end the velocity had decreased to zero, so that a small amount of catalyser had to be added to bring the reduction to an end.

To demonstrate the activating effect of the oxygen still more clearly, the hydrogen was mixed with a still far greater quantity, viz. with 4,8 % and compared with hydrogen that had been carefully purified (but evidently still containing oxygen).

2,0336 Gr. cinnamic acid-methylester hydrated with 4 ccm. sol, absorbed 391 ccm., calculated 306 ccm.

The blank experiment also with 4 ccm. Pd sol showed volume-contraction of 65 ccm. It is remarkable that this reaction i. e. the water-formation, proceeded rather slowly, the sol being completely paralysed, even after the addition of another cmm. Pd-sol.

The control-experiment with purified H_2 with a very slight oxygen-quantity was performed with 1,9958 substance, 4 ccm. Pd-sol and like the two preceding ones at 25° C. and with 2250 rotations of the spray-stirrer.

Absorbed 291 ccm., calculated 294. (This deficiency is probably to be attributed to a not inconsiderable change of temperature in the neighbourhood of the gas-burette, during the experiment, on account of which the volume-calculation has been less accurate).

The reduction took place altogether regularly without any consider-able paralysis, as a sign that the H_2 contained some O_2 after all.

Yet the difference in velocity with the H_2 containing $\pm 5\%\ O_2$ is very striking as may be seen from the subjoined table.

N⁰.	Gas-absorption of the cinnamic acid methylester	5 min.	10 min.	15 min.	20 min.	Duration of reduction	N⁰. of the graphic re-presentation
I	In H_2 with 4.8% O_2	66	120	175	230	60′	27
II	„ H_2 „ a trace O_2	25	40	52	64	180′	28
III	Combination of H_2 and O_2	20	35	44	49		29
	Difference I—III	46	85	131	181		

When we also observe, that the oxydation of the H_2 proceeds rather slowly (II) we draw the conclusion, that the two reactions: the oxydation of the H_2 and the reduction of the ester, influence each other very favourably.

This might lead us to suppose that owing to the presence of the oxygen the palladium is continually freed from a paralysis-layer, so that the number of atoms becoming available for the reduction-reaction is greater than when no O_2 is present. But if this were so, the paralysing of the catalyser, when no reducible substance is present would be unintelligible. It may be, that the solvent, the 80 % alcohol, which no doubt will be acted upon by the oxygen and converted into aldehyde, plays an important part.

A closer investigation will have to elucidate this question, but it appears at any rate that this catalytic reduction is far more complicated, than would appear at first sight.

It is certain that the velocity of the hydration proper:

$$H_2 + \text{substance to be reduced} = \text{reduction-product},$$
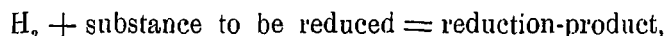
can be considerably modified by a by-reaction, so that we feel still more positive in concluding, that we have not measured the velocity of this *reaction*.

The question, whether we shall ever be able to measure this velocity of reaction when using colloidal catalysers cannot be solved yet.

It would be indispensable for us to be able to introduce these catalysers into the reaction-mixture in such a state and to bring about the course of the reaction in such a manner, that the forma-

tion of paralysis-layers is altogether excluded; but the part the oxygen has played in our experiments, gives but little hope that we shall be enabled to fulfil this condition in the near future.

§ 3. On examining the graphic representations we notice especially in those hydrations with gas-mixtures deficient in oxygen, a strong curved line, pointing to paralysis. This paralysis evidently enters sooner with the cinnamic acid aethylester than with the methylester, moreover part of the catalyser repeatedly flocked out.

To make the phenomenon stand out the more, we at first added somewhat less Pd-sol.

With N°. 23 we first used 2 ccm.; after 30' another 3 ccm. were added. Though the velocity after the second addition was very considerable, yet a strong retardation soon set in.

When starting from 1 cc.m. sol, the velocity had soon decreased to zero, but when a second cc.m. sol was added, the initial velocity was of a similar order of magnitude and occasionally even somewhat greater than if we had immediately started from 2 ccm. sol.

With a view to the ever varying quantity of oxygen we must be very cautious in drawing a conclusion. But it may be in indubitably concluded that the paralysis of the first quantity of sol does not happen to the same extent, as otherwise hardly any hydration would have set in. The first quantity of sol will probably fix an impurity of unknown nature; perhaps the second quantity can partially take on the paralysing substance from the first quantity. A closer investigation is desirable.

§ 4. With the undecylenic aethylester too, a great retardation in the second part of the hydration had been observed, during the first experiments. (N°. 4—7, without thermostat).

The same took place with the undecylenic acid when using H_2 freed from oxygen, 2.0237 gr. dissolved in 100 ccm. 80 °/₀ alcohol + 4 ccm. Pd-sol, employed 252,5 ccm. calculated 253 ccm. (N°. 30).

The first 130 ccm. were absorbed in 5 minutes, then a very pronounced retardation set in, in the following 5 min. 24 ccm. were absorbed and in the then succeeding 5 min. 16 etc.

Simultaneously a flocking-out had set in, which proved to be complete when the reduction was over.

As a solution of undecylenic acid + 4 ccm. Pd-sol remained unchanged for days, it may consequently be ascribed either to the undecylenic acid formed, to the reduction itself, or to both.

From an experiment with undecanic acid it appeared that this substance indeed, flocked out the sol in 80°/₀ alcohol.

Now a flocking-out need not necessarily cause a paralysis; but as the first phenomenon is a visible indication of the diminution of the surface of the catalyser it is most probable that in this instance the decrease of the velocity of reaction is related to the flocking-out. It stands to reason that in determining the velocities of hydration, the possibility of the paralysis must always be reckoned with, and that any cases in which flocking-out sets in are of but little value for the comparison of these velocities.

We consequently give a short summary of the substances, which at a normal temperature immediately or after a short time completely flock-out the Pd-sol:

in aqueous solution: diluted HCl, diluted KOH; in 80°/₀ alcohol undecanic acid, cinnamic acid, phenol, acrylic acid methylester, iso-crotonic acid, oleic acid, glacial acetic acid, propionic acid, butyric acid, valeric acid, capric acid, caproic acid, lauric acid, palmitic acid.

On the other hand the sol remained unchanged for a considerable time: in aqueous solution on the addition of diluted sulphuric acid, acetic acid to 80°/₀, diluted soda, undecylenic acid, undecylenic acid aethylester, cinnamic acid methyl- and aethylester. Diluted nitric acid dissolved the metal.

On summarising the phenomena described in these pages, we undoubtedly get an idea, that even in this apparently so simple catalytic reduction, viz. an irreversible reaction with an elementary catalyser, the events are far more complicated and far more sensitive to by-circumstances than could be expected.

Not until these events have been sufficiently studied, so that they can be entirely brought under the control of the experiment, can a mathematical treatment produce good results.
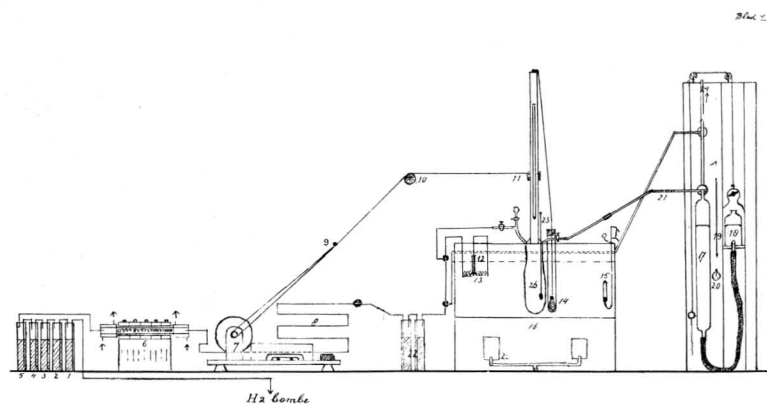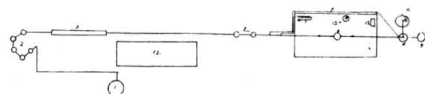
Fig. 1.

1. H_2 bomb.
2. Rinsing-flasks.
3. Cu-tube.
4. H_2SO_4 rinsing-flasks.
5. Glass spiral to saturate Pdsol with H_2.
6. Hydrogenation-apparatus.
7. Circulation-tube for the H_2.
8. Gas-burette.

9. Mercury-flask.
10. Escape-tube for the H_2.
11. Cup-shaped glass with water in which the
    escape-tube empties.
12. Motor.
13. Thermometer in the thermostat.
14. Electric lamp „   „   „
15. Thermo-regulator.

Fig. 2.