Chemistry. — *"The stability of cyclo hydrocarbons in connection with their configuration. The transformation of cyclo-hexene into benzene and cyclo-hexane."* (Contribution to the knowledge of catalytic phenomena). By Prof. J. Böeseken and K. H. A. Sillevis. (Communicated by Prof. A. F. Holleman.)

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1. When studying the stability of hydrocarbon compounds below 400° and in the presence of catalysts account must be taken of the fact that under those circumstances there is only one real stable equilibrium [1]) namely

$$CH_4 \gtrless C \text{ (graphite)} + 2H_2,$$
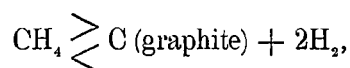
which, below 400°, is practically situated entirely at the methane side.

Hence, if this gas is generated from an arbitrary hydrocarbon, this will be a proof that the catalyst employed is capable of causing the real equilibrium under the conditions of the experiment.

Experience has now taught that under the influence of definite conditions, transformations may occur and equilibria be possible without methane being evolved or carbon being separated.

All these latter equilibria are metastable and the possibility of their realization is closely connected with a judicious choice of conditions and catalyst. In order to choose properly we must first ask which catalysts are the most suitable for definite changes. [1])

In the hydrocarbons we are dealing with three kinds of bonds: the C-C-, the C-H-, and the H-H-bond. In order to attain the real equilibrium the catalyst must be able to exert an action on all bonds (to effect a dislocation) [2]) which is only possible when, under the conditions of the catalysis, it does not unite to form stable compounds with the elements or combinations thereof which are to be "activated".

On the other hand they should be substances which, under somewhat modified conditions, can unite with carbon as well as with hydrogen (H. J. Prins). [3])

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1) M. Mayer and V. Altmayer. B **40**, 2134 (1907); v. Wartenberg Z. ph. Ch. **61**, 366 (1908) **63**, 269 (1909).

2) I refer to the dissertation from H. J. Prins, Delft 1912, wherein, supported by the principle of reciprocity, he has endeavoured to give an explanation of the catalytic phenomena.

3) Recueil **29**, 86 (1910).

Substances which are most suitable for this purpose are metals which form carbides as well as hydrides. Their catalytic action will be the most powerful[1]) in the region where these combinations exist in a condition of dissociation, where, consequently the "activation" is greatest without the catalyst being paralyzed by too great a chemical action.

To these metals appear to belong in the first place nickel and cobalt (MAIER and ALTMAYER l.c.); to their action must be attributed the fact that during the hydrogenations according to SABATIER and SENDERENS [1]) considerable quantities of methane are often formed.

The activating power of a catalyst will, however, have to be unequal, under the same conditions, for each of the bonds, because the dissociation regions of the carbides and the hydrides will not as a rule coincide, and experience has taught that nickel is eminently suited for the hydrogenation of hydrocarbons without methane being evolved, if only we keep below ± 240°.

Hence, the C-C-activation of nickel at the ordinary pressure only appears to become appreciable above that temperature, which we may call the catalytic limit for that bond. Little is known of the limit of the hydrogen activation of nickel, which seems to be greatly dependent on the condition of the metal, anyhow the temperatures at which this activation becomes important and the hydrocarbon activation limit do not diverge greatly.

In the case of other metals these limits may differ more seriously. This is shown in a very convincing manner from the research of ZELINSKY [2]). He demonstrated that palladium black, which at 0° is an excellent hydrogen "activator" did, at 300°, resolve cyclo-hexane into benzene and hydrogen only ; the catalytic limit of palladium black for the C-C-bond of cyclo-hexane is therefore situated above 300°.

Hence, if we wish to study the resolving or combining reactions of a hydrocarbon and hydrogen, palladium black is the catalyst *per excellence.* [3]).

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[1]) Compare Ann. Ch. et Ph. [8] 4, 336 (1905).

[2]) B 44, 3122 (1911); 45, 3678 (1912).

[3]) In reality, at least two bonds are activated simultaneously, for instance the C H and the H H bond or the C-C and the other bonds; in order not to become too prolix we will distinguish provisionally the carbon and hydrogen activation only. Under carbon activation I, therefore, understand here the influence which is not limited to causing a dislocation but leads to a dissociation of the saturated carbon-carbon bond. Before this point is attained some activation still takes place but this can lead at most to linking and splitting off of hydrogen; hence to simplify matters I am speaking in that case only of hydrogen activation.

2. By this happy choice of catalyst, ZELINSKY showed that benzene and cyclo-hexane, at ± 200° and at the ordinary pressure, are related according to the mobile equilibrium:

$$C_nH_{2n} \gtrless C_nH_{2n-6} + 3H_2,$$
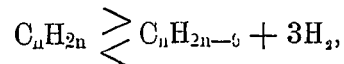
which, above 300° is shifted entirely in the direction of benzene and hydrogen, and below 170° wholly in the direction cyclo-hexane.

From this follows that at 300° cyclo-hexane is *super*saturated, that six carbon atoms which are linked together are no longer *tetra*valent but *tri*valent in regard to the hydrogen. It is true the benzene at the ordinary temperature is unsaturated for hydrogen, but if we take into consideration that the decomposition of cyclo-hexane starts at 170° that unsaturation cannot be considerable.

The knowledge of this equilibrium enables us to understand why the aromatic compounds are reduced with difficulty and why they behave somewhat like saturated hydrocarbons; without a catalyst like palladium black we could not have elucidated the matter experimentally.

Nickel would have been less suitable because below 100° it is but little hydrogen-active and also because not far above 300° it becomes too much carbon-active.

One of us [1]) has pointed out that the great general stability of the aromatic compounds, to which belongs this little-pronounced unsaturation, can be deduced from the "Werner principle of affinity distributed evenly in space" when we take into consideration the extraordinary favourable steric distribution of the atoms. This stability can differ very little from that of the hydroaromatic compounds because the distribution in space is more favourable.

He also considered the question why, in substitutions in the benzene nucleus the additive products to be expected have as yet not been isolated. These ought to be derivatives of di- or tetrahydrobenzene.

If we consider these hydrocarbons themselves we notice that here is found an unequal distribution of the unsaturation as well as of the atoms in space; in the presence of suitable catalysts they ought to be converted more readily into benzene or cyclo-hexane than the two latter into each other.

Guided by these considerations we have studied in the first place the behaviour of cyclo-hexene. As stated above, this hydrocarbon

[1]) Proc. March 1912.

will not only be much more unsaturated than benzene, which fact has long been known, *it must also be much more supersaturated than cyclo-hexane and be converted into -benzene under conditions where cyclo-hexane does not yet lose hydrogen* thus, for instance at 180° and in the presence of a suitable catalyst. For this purpose we have passed cyclo-hexene over nickel at 180° in a current of carbon dioxide and indeed obtained a considerable quantity of benzene (with cyclo-hexane)[1].

The labile cyclo-hexene will begin to split into benzene and hydrogen:

$$C_6H_{10} = C_6H_6 + 2H_2 ,$$

but this hydrogen will subsequently form cyclo-hexane with the still undecomposed cyclo-hexane; the whole process thus progresses:

$$3\,C_6H_{10} = C_6H_6 + 2\,C_6H_{12} .$$

Hence, according to this equation a mixture of 33.3°/₀ of benzene and 66.6°/₀ of cyclo-hexane should have formed; in reality we found about 40°/₀ of benzene while 2 à 4°/₀ of cyclo-hexene had remained unchanged; the remainder consisted of cyclo-hexane.

The fact that too much benzene has been found here may be due to different causes. First of all, the decomposition of cyclo-hexane into benzene and hydrogen starts already at 180° (ZELINSKY l.c.); true, we have found no hydrogen in the reaction products but we found CO, which may have been generated by reduction of the CO_2.

This formation of CO points, however, to the fact that, in this case, the CO_2 must not be looked upon as an indifferent gas, so that the experiments will have to be repeated in a current of nitrogen. Although the vapours evolved were cooled by means of solid carbon dioxide and alcohol there is still a chance that a little has been lost by evaporation which may also be a possible source of an excess of benzene.

In any case the supersaturation of the system C_6H_{10} in regard to $C_6H_6 + 2\,H_2$ has been proved sufficiently.

It now speaks for itself that, in the hydrogenation of benzene according to SABATIER and SENDERENS, substances like cyclo-hexane — even supposing them to be actual intermediate products — cannot be retained. When they are converted almost completely into benzene and cyclo-hexane in an atmosphere of CO_2 nothing is to be expected, in presence of an excess of hydrogen, but cyclo-hexane mixed

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[1] For this we have chosen for practical reasons nickel and not palladium particularly because, as a matter of fact, we kept far below 240°.

At the ordinary temperature Pd. and Pt. were not active enough to promote the transformation.

eventually with benzene (if working above 180°) and with methane- if working above 240°.

3. As regards the experimental part, the cyclo-hexane was prepared from cyclo-hexanol[1]) by slowly distilling this, according to Brunel[2]), with dried and powdered $KHSO_4$ (80 grams to 200 grams of $C_6H_{11}OH$) from a flask with a high adapter and then fractionating the distillate:

A liquid $Bp._{76} = 82°.5—83°.5$; $D_4^{20} = 0.8120$; $n_D^{18} = 1.44617$ was obtained.

In glacial acetic acid it rapidly took up bromine so that in presence of benzene and cyclo-hexane it could be titrated with the same.

260,4 mg. of cyclo-hexene mixed with 1 gr. of C_6H_6 and 2 gr. of C_6H_{12}
consumed 510 mg. of Br_2 calculated 508 mg.

298.6 gr. with 1.5 gr. of C_6H_6 and 1 gr. of C_6H_{12}
consumed 584.5 mg. of Br_2, calculated 582 mg.

Subsequently a certain weight was passed slowly and in a feeble current of CO_2 over active nickel heated at 180°. We used the apparatus that had been employed for the decomposition of oenanthol[3]) with this understanding, however, that the CO_2 was first carefully freed from oxygen and that the vapours leaving the electric ' oven were first cooled by ice and salt and then by alcohol and solid carbon dioxide to be finally drawn into an aspirator. The cyclo-hexene was dropped at the beginning of the oven from a small capillary pipette in such a manner that the minute droplets arrived in the tube at the spot where the carbon dioxide was introduced.

First of all, the products obtained were tested qualitatively.

The liquid obtained had a pronounced odour of benzene, whereas the characteristic odour of the hexene had all but disappeared; it was cautiously nitrated with a mixture of sulphuric and nitric acid, the product obtained after being washed was fractionated; the fraction passing over below 100° was freed from nitrobenzene by means of tin and hydro-chloric acid; it now distilled at 80°, solidified at 5,°5 and had the agreeable odour of cyclo-hexane.

The fraction boiling above 100° was converted into aniline and identified as such.

A few quantitative determinations were then made, that is to say, it was determined how much bromine was taken up in a glacial

[1]) This latter according to HOLLEMAN Recueil 24, 21 (1905).

[2]) Bull. [3] 33, 270, also WILLSTÄTTER B. 45, 1464 (1912).

[3]) Recueil 32, 27 (1913).

acetic acid solution in order to ascertain the content of unchanged cyclo-hexene; the hydrogenation figure was then determined according to WILLSTATTER's method, with active-platinum in glacial acetic acid from which, after deducting the hydrogen required for the reduction of the cyclo-hexene, the benzene content could be deduced, and finally the density and refraction were determined by way of control.

The subjoined table gives a survey of the results obtained.

TABLE.

Substance	Bromine number expressed in mg. p. gram of substance	Reduction number expressed in cc H_2 per gr. of substance	Condition of the product calculated therefrom			d_4^{20}		n_D^{20}	
						found	calculat.	found	calcul.
Cyclohexene	1950	270	—			0.8120		1.44617	
Benzene	0	852	—			0.8790		1.50042	
Cyclohexane	0	0	—			0.7810		1.42691	
			C_6H_{10}	C_6H_6	C_6H_{12}				
Reaction prod. I	68	345	3.5%	39.4%	57.1%	0.8194	0.8207	1.46161	1.4564
„ „ II	77	376	4.0%	41.7%	54.3%	0.8189	0.8231	1.46310	1.4583
„ „ III	95	—				0.8153		1.45962	

The gas drawn into the aspirator contained considerable quantities of carbon monoxide; methane was not present.

4. In our general consideration we have assumed that at 180° and in the absence of an excess of hydrogen, benzene and cyclo-hexane only could be present in admixture with methane; we must, however, also keep account of the presence of methylcyclo-pentane, the isomer of cyclo-hexane with the stable saturated 5-ring.

Nothing is known as to the relation of these two isomers at the ordinary pressure.

ASCHAN[1]) certainly has found that from 70 grams of C_6H_{12}, after this had stood for two days with 140 grams of anhydrous $AlCl_3$ and was then boiled for 48 hours — were obtained 2.5 grams of a fraction boiling below 78°, which fraction was saturated and possessed the general formula $C_n H_{2n}$; from this we can at most draw the conclusion that it may have contained methylcyclo-pentane and that the two isomers may be capable of existing for

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[1]) Ann. **324**, 12 and 85 (1902).

some time in the presence of an immense excess of aluminium chloride.

A transformation of cyclo-hexane or of a mixture of benzene and hydrogen into methylcyclo-pentane at a high pressure and temperature has been observed, however by IPATIEW and KIŽNER.

IPATIEW[1]) heated quantities of 40 grams of C_6H_{12} with 3 grams of Al_2O_3 at 500—510° and under a pressure of 70 atm. and could liberate from a total of 700 grams a little of the cyclo-pentane derivative; in addition a great many aromatic compounds and unsaturated hydrocarbons had formed.

Also this experiment does not say much more but that the hydro-carbons are possible in presence of each other which, moreover, does not signify much as, like in ASCHAN's investigation, there is here no question whatever of an equilibrium attained. Both experiments prove that Al_2O_3 and $AlCl_3$ are bad catalysts for the saturated carbon-carbon bond, which could not be expected to be otherwise [2]).

Of much more importance is the observation that benzene is converted into methylcyclo-pentane when it is heated at 280° in a sealed tube with an excess of HI [3]) because from this it follows that at 280° and under pressure the cyclo-pentane derivative is more stable than the cyclo-hexane or the mixture of C_6H_6 and hydrogen.

Of a pure catalysis there is, however, also no question in this case as a very large excess of III and I, has been employed here; moreover, this superior action of iodine over $AlCl_3$ is in harmony with the fact that the element can unite with hydrocarbons as well as with hydrogen to form dissociable compounds under conditions which are not far removed from that of the discussed transformation (H. J. PRINS l.c.)

In order to study the relation of the two isomers at the ordinary pressure we will have to choose in any case a C-C-activator such as nickel even if we run the risk that a part of the system attains the methane equilibrium.

The fact that not much methylcyclo-pentane can have formed in the transformation of the cyclo-hexene into benzene and cyclo-hexane at 180° as studied by us, is, moreover, shown from the

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[1]) B. **44**, 2987 (1911).

[2]) On the other hand the large quantities of higher condensation products of an aromatic character show that $AlCl_3$, in particular, activates the unsaturated bonds. As soon as a saturated hydrocarbon begins to lose hydrogen, under the influence of $AlCl_3$ this property must lead to the actually observed complications.

[3]) N. N. KIŽNER. Cent. Bl. 1897 II, 344.

figures found for density and refraction. These are for the naphtène: $d_4^{19.5} = 0.7488$ and $n_D^{19.5} = 1 4096$ [1]), hence, much smaller than that of cyclo-hexene.

Now, the densities found by us are certainly somewhat below the calculated ones, but on the other hand the indices of refraction are somewhat higher. Moreover, the product freed from benzene by nitration had almost the true solidifying point of cyclo-hexane whereas this suffers a very strong depression by the presence of admixtures [2]). Hence, after the nitration, these cannot have been present in quantities exceeding 1 %.

SUMMARY.

1. Cyclo-hexene at 180° and ordinary pressure is metastable in regard to the corresponding mixture of benzene and cyclo-hexane.

2. Cyclo-hexane at 300° and ordinary pressure is metastable in regard to the corresponding mixture of benzene and hydrogen (ZELINSKY). Six cyclo-combined carbon atoms are then trivalent in regard to the hydrogen.

3. Cyclo-hexene at 180° and ordinary pressure is metastable in regard to the corresponding mixture of benzene and hydrogen.

4. Cyclo-hexene is more strongly *super*saturated with hydrogen than cyclo-hexane.

5. Probably, methylcyclo-pentane at 280° and under pressure is more stable than the corresponding mixture of benzene and hydrogen or cyclo-hexane.

6. Nickel is, in the first place, a hydrogen activator; the carbon activation becomes only considerable at 240°; at 180° this latter action in regard to the first may be neglected.

7. Palladium is an excellent hydrogen activator, the carbon activation may still be neglected at 300° (ZELINSKY).

8. Iodine at 280° and under pressure is presumably a strong hydrogen and a feeble carbon activator [3]).

[1]) ZELINSKY. B. 35, 2684—86 (1902).

[2]) MASCARELLI states a molecular depression of about 200 (Atti R [5] 16 I 924 (1907); thi value we obtained also in the determination of the melting line of the system C_6H_6—C_6H_{12} which consequently takes a very asymmetric course.

[3]) See Pat. Kl-o 250236 3/8 1910, Zentr. Bl. 1912 II 1084.