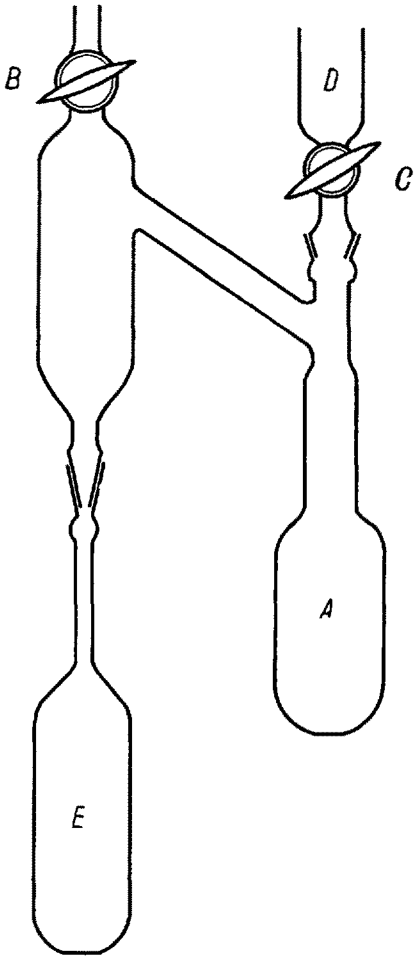
of lactic acid. This reaction goes well on a small scale only if one takes advantage of the heat of the reaction by compressing the mixture of $BaCO_3$ and Mg powders into a hard, dense mass. In practice, ·2 g of $BaCO_3$ was intimately mixed with ·5 g of Mg powder, and the mixture compressed in a steel pellet press to a small wafer. This was placed in an iron boat inside an iron pipe through which a stream of H_2 gas was flowing, and was then set in a furnace at 1,000°. When the temperature of the pipe reached 700–750° reaction occurred and the pellet exploded. The pipe was cooled rapidly with water and the gray-black contents of the boat transfered to the apparatus shown in the Figure for conversion to acetylene. Acetylene titrations according to WILLSTÄTTER[1] indicated yields of 75–85% in this step.



Glass apparatus for converting BaC_2 to acetate.

Conversion of BaC_2 *to Acetate*: BaC_2 reacts rapidly and quantitatively with water to yield acetylene. The method then used for acetate formation was based upon an observation by FEUCHTER[2] that acetylene bubbled through molten NaOH—KOH was partially converted to acetate. This principle was adopted by STROSACKER *et al.*[3] who used solid NaOH in the commercial production of acetate. We found a practically quantitative conversion when acetylene was heated in a sealed tube with alkali-saturate asbestos.

The apparatus shown in the Figure proved convenient for carrying out the reaction. In practice, the BaC_2 was placed in *A*, 15 ml water in *D*, and ·3 g of asbestos upon which had been dried ·6 g KOH in *E*. The apparatus was evacuated through stopcock *B* and a liquid air flask placed around *E*. Water, admitted through stopcock *C*, reacted violently with the carbide (the mixture was warmed with a flame for 5–10 minutes to insure completeness) and the evolved acetylene plus some water condensed in *E*. Tube *E* was sealed off and placed in a furnace at 250° for 1 hour, after which the contents were suspended in 50 ml water, 6 ml of 20% H_2SO_4 were added, and the acetic acid was distilled out. The acid was identified by a Ducleaux titration. Yields of 80–90% were obtained in this conversion; overall yields from $BaCO_3$ being in the range of 60–80%.

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Karolinska Institute, Chemistry Department, Stockholm, September 12, 1947.

Zusammenfassung

Es wird eine Methode beschrieben, mit deren Hilfe sich aus $BaCO_3$ Essigsäure herstellen läßt, die C^{13} oder C^{14} symmetrisch als «tracer» enthält: $BaCO_3$ wird zunächst zu BaC_2 reduziert. Hierfür wird $BaCO_3$ in einer kleinen Kugel mit Magnesiumpulver gemischt und gepreßt und dann in reiner Wasserstoffatmosphäre auf 700–750° erhitzt. Das resultierende Karbid (BaC_2) wird langsam mit Wasser zersetzt und damit Azetylen gewonnen. Das Azetylen wird mit Hilfe von mit Kaliumhydroxyd durchtränktem Asbest auf 250° erhitzt, wobei sich Kaliumazetat bildet. Dieses Kaliumazetat in Asbest wird in Schwefelsäure suspendiert. Durch Destillation erhält man Essigsäure. Die Ausbeute beträgt etwa 60–80%.

On the Mechanism of Catalytic Hydrogenation and Dehydrogenation with Rhodium[1]

The successful use of synthetic high polymers in the preparation of highly active noble metal catalysts led to the extension of their application to rhodium. Following the earlier[2] procedure for palladium and platinum we have prepared a rhodium-polyvinyl alcohol catalyst (Rh-PVA).

The Rh-PVA catalyst was used in the hydrogenation of the $C=C$ double bond and NO_2 group. In particular, nitrobenzene[3] was studied in greater detail. It is readily reduced to aniline at atmospheric pressure and room temperature by shaking its alcoholic solution with hydrogen in the presence of Rh-PVA. Addition of hydrogen to the carbon-carbon double bond is also easily achieved.

The behaviour of palladium and rhodium is remarkably different in that the activity of rhodium is greatly

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[1] R. WILLSTÄTTER and E. MASCHMANN, Ber. dtsch. chem. Ges. *53*, 939 (1920).

[2] H. FEUCHTER, Chem.-Ztg. *38*, 273 (1914).

[3] C. J. STROSACKER, C. C. KENNEDY, and E. L. PELTON, U. S. Patent 1866430 (1932).

[1] Contribution No. 57.

[2] F. F. NORD et al., J. Am. chem. Soc. *63*, 2745, 3268 (1941); *64*, 2721 (1942); *65*, 429, 2121 (1943); *66*, 2126 (1944); Proc. Nat. Acad. Sci. U. S. *29*, 246 (1943). – H. S. TAYLOR and W. J. SHENK, J. Am. chem. Soc. *63*, 2756 (1941); T. H. JAMES, ib. *64*, 732 (1942).

[3] F. F. NORD, Ber. dtsch. chem. Ges. *52*, 1705 (1919).

affected by the p_H of the solvent and other functional groups, whereas the activity of palladium is little or not influenced (Tables I and II).

Table I

Influence of p_H on the rate of reduction of nitrobenzene

p_H	$k \cdot 10^5$	
	Rh	Pd
3	0·69	1·62
7	0·30	1·62
10	1·38	1·57

Table II

Influence of substituents on the rate of reduction of nitrobenzene

Substance	$k \cdot 10^6$	
	Rh	Pd
p-CN	11·1	18·9
p-CHO	10·8	18·7
p-NO_2	10·4	18·5
p-COOH	10·1	18·5
p-I.	9·25	18·5
p-Cl	9·02	18·5
p-Br	8·79	18·5
None	8.33	18·5
p-OCH_3	6·25	18·5
p-NH_2	1·85	18·5

These striking differences suggest that the mechanisms of hydrogenation with Rh-PVA and Pd-PVA may be different. A series of substituted nitrobenzenes (Table II) and propylene derivatives (Table III) were studied. The reduction of the NO_2 group with Rh is accelerated by electron-attracting para-substituents, while it remains unaffected in the case of Pd. With propylene derivatives, hydrogenation of C=C with Rh is favored by the polarity of the adjacent groups.

Table III

Influence of adjacent groups on the hydrogenation of C=C

Compound	$k \cdot 10^5$ (Rh)
Allylamine	3·12
Acrylic acid	2·63
Acrylonitrile	2·12
Allyl alcohol	2·08
Allyl acetate	1·94
Allyl ethyl ether	·97
Acrolein	·28

The results indicate that rhodium *ionizes* molecular hydrogen, the positive H^+ being the effective starting agent[1]. Palladium, on the other hand, seems to form *atomic* hydrogen $H^\cdot$. These assumptions are supported by a stepwise reduction of nitrobenzene, by the electronic configurations of Pd and Rh atoms and by the different nature of the adsorption of hydrogen by these metals.

The Rh-PVA catalyst is effective also in the *de*hydrogenation of formic acid and isopropyl alcohol at 95 °C. The presence of elementary sulfur increases the rate of dehydrogenation. Kinetic studies show that there is a stoichiometric relationship between rhodium and sulfur:

Table IV

Rate of decomposition of HCO_2H by Rh (5 mg) in the presence of S

Amount of S (mg)	cm³ of gas evolved in minutes			
	5	10	15	20
0	5	6·5	7·5	flocc.
1	7	11	12	flocc.
2	9	16	23	27
5	19	27	37	45

The influence of sulfur was also studied in the hydrogenation of maleic acid and nitrobenzene in order to correlate the mechanisms of hydrogenation and dehydrogenation. Sulfur proved to be toxic in the former case.

The available evidence regarding the interaction of sulfur points to a twofold rôle: (1) Sulfur in conjunction with rhodium may act as a hydrogen acceptor[1], hydrogen being subsequently liberated in molecular form and combined with sulfur as H_2S whose presence has been detected. (2) An intermediate complex (S-Rh-H-substrate) is apparently formed. The attachment of sulfur to the rhodium atom weakens the -H-substrate linkage.

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Zusammenfassung

Mit Hilfe eines neuen Rhodiumpolyvinylalkohol-Katalysators wurde der Mechanismus katalytischer Hydrierungen und Dehydrierungen untersucht. Aus den mitgeteilten Versuchsergebnissen geht hervor, daß molekularer Wasserstoff durch Rhodium *ionisiert* wird, während mit Palladium *atomarer* Wasserstoff gebildet wird. Bei der Untersuchung von Dehydrierungen wurde festgestellt, daß diese Reaktionen in Gegenwart von elementarem Schwefel beschleunigt werden. Der Schwefel wirkt entweder als Wasserstoffakzeptor oder nimmt an einer Komplexbildung teil.

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[1] R. KUHN, Naturwiss. *13*, 171 (1925).

[1] L. J. SCIARINI and F. F. NORD, Arch. Biochem. *3*, 261 (1943).

Diffusionsmessungen an Kautschuk

Hochmolekulare Stoffe zeigen unter einer *äußeren* mechanischen Beanspruchung ganz besondere, eigentümliche Effekte; es liegt deshalb nahe, auch das *innere* mechanische Verhalten, im speziellen die innere Beweglichkeit dieser Stoffe zu untersuchen. Prinzipiell kann dies unter anderem in der Weise geschehen, daß man *fremde* Teilchen, insbesondere solche von molekularen Abmessungen als Sonden in das zu untersuchende Material einbringt und ihre Beweglichkeit bestimmt; prak-