adjust the manometer to the reference point; note the pressure reading.

6. Open stopcock M; raise carefully the mercury in the burette up to the higher reference point; N_2 condenses in the pycnometer.

7. Close stopcock M; note the pressure reading.

Actions 4 to 7 are repeated until the pycnometer is nearly filled with liquid nitrogen. Condensation of the final quantity must take place at a pressure which is not more than 1–2 cm higher than the condensation pressure. This is carried out by raising the mercury in the burette very slowly.

When the liquid nitrogen level reaches the mark in the pycnometer stem (to be determined visually), stopcock M is closed. The mercury in the burette is adjusted at the lower reference point and the pressure reading noted.

The volume of the pycnometer empty or filled with as much solid material as possible is calculated from the difference between the total quantity of gaseous nitrogen added and the quantity of gas, which is not condensed at the end point. It is necessary to keep both burette and Dewar vessel at constant temperature.

At a total pressure of 780 mm Hg the condensation temperature of nitrogen is 77.6°K. At this temperature the conversion factor for gaseous to liquid nitrogen is 1 ml of N_2 (STP) $\sim 15.486 \times 10^{-4}$ ml of liquid N_2.

Some Examples

In the following table some of our density measurements of nonporous substances are given:

	Density in liquid nitrogen (g/ml)	Density in methanol (g/ml)
Spheron-2700°	1.952	1.938
Sterling FT-2700°	2.151	2.150
Aerosil	2.289	2.253

The obtained results were reproducible up to 0.2%, but a higher precision is obtainable when more care is bestowed on the pressure and temperature measurements. Limiting factors are quality of the manometer, accuracy of temperature control, and end point determination.

Other applications might be density measurements with the aid of other very volatile, expensive, or poisonous fluids. The fluid has to be gaseous at room temperature. If a suitable refrigerant is available, density measurements with liquid NH_3 will be possible; this might be interesting because the molecule is rather small (3.08 Å). Measurements with neopentane (boiling point 9.5°C) will be rather easy with this measuring device, if the pycnometer is thermostated at a temperature between 0° and 9°C. The apparatus can also be used to carry out density measurements of liquids, if a gauged pycnometer is applied.

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B. Moses

Chemical Laboratory of the
National Defence Research Organization TNO,
Rijswijk (ZH), The Netherlands
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Homogeneous Hydrogenation Using Platinum-Tin Complexes

Complexes (*1*) prepared from chloroplatinic acid and stannous chloride in a molar ratio of 1:10 in methanol have been reported (*2*) to catalyze the homogeneous hydrogenation of ethylene at room temperature and atmospheric pressure. So far the system was considered (*3*) to be unsuited for the hydrogenation of higher olefins under the above conditions. Recently partial hydrogenation of some unsaturated fatty acid esters has been achieved (*4*), by operating at higher pressure and temperature, however. At the same time platinum-tin complexes are known (*5*, *6*) as active isomerization catalysts.

TABLE 1

HYDROGENATION OF CYCLOHEXENE WITH PLATINUM-TIN CATALYSTS[a]

Expt. no.	Solvent	Platinum/tin molar ratio	Water concentration (mole liter^{-1})	Promoting additive (mole liter^{-1})	Pseudo-first order rate constant[b] (sec^{-1} × 10^4)
1	iso-C_3H_7OH	1:6	0.15 *M*	—	0.05
2	iso-C_3H_7OH	1:6	0.15 *M*	HCl 0.15 *M*	3.3
3	iso-C_3H_7OH	1:10	0.22 *M*	HCl 0.15 *M*	0.05
4	iso-C_3H_7OH	1:7	0.17 *M*	HCl 0.15 *M*	2.4
5	iso-C_3H_7OH	1:5	0.13 *M*	HCl 0.15 *M*	4.3
6	iso-C_3H_7OH	1:4	0.12 *M*	HCl 0.15 *M*	0.33
7	iso-C_3H_7OH	1:6	1.00 *M*	HCl 0.15 *M*	0.42
8	iso-C_3H_7OH	1:6	0.15 *M*	HCl 0.05 *M*	0.63
9	iso-C_3H_7OH	1:6	0.15 *M*	HCl 0.10 *M*	2.3
10	iso-C_3H_7OH	1:6	0.15 *M*	HCl 0.23 *M*	3.3
11	iso-C_3H_7OH	1:6	0.15 *M*	LiCl 0.15 *M*	0.86
12	iso-C_3H_7OH	1:6	0.15 *M*	HBr 0.15 *M*	2.3
13	iso-C_3H_7OH	1:6	0.50 *M*	HBr 0.15 *M*	4.2
14	iso-C_3H_7OH	1:6	1.00 *M*	HBr 0.15 *M*	10.0
15	iso-C_3H_7OH	1:6	5.00 *M*	HBr 0.15 *M*	0.29
16	iso-C_3H_7OH	1:6	0.15 *M*	LiBr 0.15 *M*	2.0
17	CH_3OH	1:6	0.15 *M*	HCl 0.15 *M*	0.26
18	C_2H_5OH	1:6	0.15 *M*	HCl 0.15 *M*	1.8
19	*n*-C_3H_7OH	1:6	0.15 *M*	HCl 0.15 *M*	2.4
20	*n*-$C_5H_{11}OH$	1:6	0.15 *M*	HCl 0.15 *M*	2.2
21	2-ClC_2H_4OH	1:6	0.15 *M*	HCl 0.15 *M*	1.7

[a] Temperature, 25°C; atmospheric H_2 pressure; 10 mmoles of cyclohexene in 60 ml of solvent; catalyst prepared from $SnCl_2 \cdot 2H_2O$ and 0.5 mmole of $H_2PtCl_6 \cdot 6H_2O$.

[b] By least-squares treatment.

Using cyclohexene as a standard substrate we examined the influence of several variables on the rate of hydrogenation. Experiments were carried out in a stirred glass reactor with thermostat jacket. Kinetics were studied by GLC analysis of samples as well as by measuring the rate of uptake of hydrogen.

It was found that the platinum-tin complexes represent efficient catalysts for the hydrogenation of cyclohexene, provided (i) the proper platinum/tin ratio is used, (ii) extra chloride or bromide ions are added, and (iii) solvents other than methanol are applied. Some results are collected in Table 1.

Most hydrogenations were found to be first order in cyclohexene; some examples are shown in Fig. 1. The role of the concentration of the complex and the hydrogen in the rate expression is under investigation.

The effect of variation of the platinum/tin ratio is demonstrated by Experiments 2–6; optimal rate was obtained when applying a ratio of 1:5. This might be taken as evidence for a pentacoordinated platinum (*7*) in the active complex. The presence of a large excess of competing tin ligands retards the hydrogenation.

The addition of hydrochloric or hydrobromic acid to the catalyst resulted in a sharp rise in reaction rate. A considerable increase in activity was also brought on by the addition of lithium chloride or bromide. In both cases the bromine promoter was the most effective. In these promoted catalysts the presence of $SnHal_3^-$ ligands is expected.

Differences in the amount of water present produced fairly large effects on rate, as shown by Experiments 2, 7, 12–15. Unlike the HCl-activated catalyst the HBr-promoted complex required a 1 *M* water concentration for maximum activity.

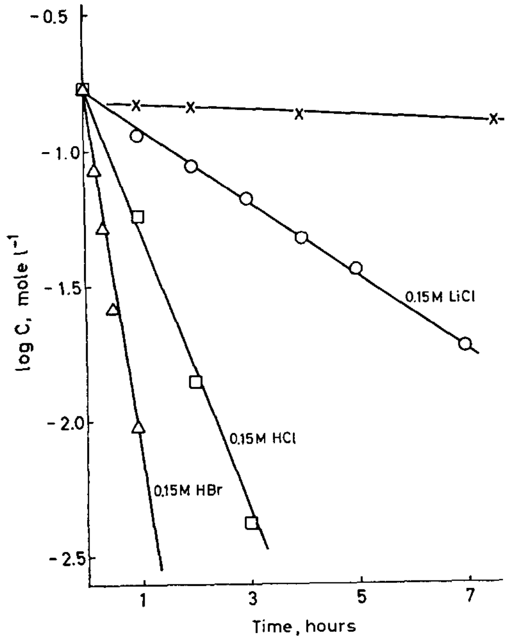

FIG. 1. Plots of log cyclohexene concentration versus time for hydrogenation of cyclohexene in isopropyl alcohol at 25°C: ×, Expt. 1; ○, Expt. 11; □, Expt. 2; △, Expt. 14; cf. Table 1.

Of several alcoholic solvents tested (Experiments 2, 17–21) isopropyl alcohol gave the best performance. Differences in H_2 solubilities may contribute here, but cannot account for the low rate in methanol.

Using promoted platinum-tin catalysts it appeared possible to perform the homogeneous hydrogenation of various other olefinic compounds. Rate of hydrogenation was found to depend strongly on the degree of substitution of the double bond, the order or reactivity being terminal > 1,2-disubstituted > trisubstituted.

This feature enabled selective hydrogenation of suitable dienes. We mention the hydrogenation of some 2-alkyl-2,5-cyclohexadiene-1-carboxylic acids to 2-alkyl-2-cyclohexene-1-carboxylic acids.

As might be expected, isomerization may constitute a competing reaction. For example, when hydrogenating methylenecyclohexane with a HCl-promoted complex the rates of hydrogenation and isomerization (to 1-methylcyclohexene) were in the proportion of 15:1.

Finally, using the above platinum-tin complexes we observed a smooth and selective homogeneous hydrogenation of carbon–carbon triple bonds.

The mechanism of these hydrogenations is under investigation.

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H. VAN BEKKUM
J. VAN GOGH*
G. VAN MINNEN-PATHUIS

Laboratory of Organic Chemistry
Technische Hogeschool
Delft
The Netherlands
Received November 22, 1966

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* Present address: Koninklijke/Shell-Laboratory, Amsterdam.