Homogeneous Hydrogenation with Platinum-Tin Chloride Complexes as Catalysts

Some years ago it was found by Cramer *et al.* (*1*) that ethylene and acetylene can easily be hydrogenated homogeneously at room temperature and atmospheric hydrogen pressure, using a platinum-tin complex as a catalyst. Methanol was used as a solvent for the complex. It would be very difficult to hydrogenate higher alkenes in the system applied by these authors. This was confirmed by Bond and Hellier (*2*) who applied this catalyst system for the isomerization—in a hydrogen medium—of 1-pentene. Bailar and Itatani (*3, 4*) hydrogenated higher unsaturated hydrocarbons at a high hydrogen pressure (35–73 atm) and temperatures between 30°–90°C using catalyst systems such as $H_2PtCl_6 + SnCl_2 \cdot 2H_2O$, $H_2PtCl_6 + SnCl_2 \cdot 2H_2O + HCl$ and $\{(C_6H_5)_3P\}_2PtCl_2 + SnCl_2 \cdot 2H_2O$ dissolved in a mixture of benzene and methanol. In this way the methyl esters of soyabean oil and methyl linoleate were hydrogenated. A similar type of catalyst ($\{(C_6H_5)_3P\}_2PtHCl + SnCl_2 \cdot 2H_2O$) was used by Jardine and McQuillin (*5*) for the homogeneous hydrogenation of, e.g., norbornadiene.

We have now found that in solvents other than methanol or its homologs, the platinum-tin chloride complex formed from $H_2PtCl_6 \cdot 6H_2O$ and $SnCl_2 \cdot 2H_2O$ is very suitable as a homogeneous hydrogenation catalyst at atmospheric pressure and room temperature. For example, the aliphatic carboxylic acids (with the exception of formic acid) and their esters are extremely suitable as a solvent for the complex in the homogeneous hydrogenation of various unsaturated substrates. Figure 1 shows the course of the hydrogenation of 1-hexene using glacial acetic acid as solvent. In this experiment, 1-hexene disappears according to a first order reaction in which $k_1 = 1.08 \times 10^{-4}$ sec^{-1}. In addition to hydrogenation isomerization takes place. The formation of a large amount of 2-*trans*-hexene is remarkable (Fig. 1). The same effect has already been observed by Bond (*2*). From experiments with 2-hexene, it has become clear that the hydrogenation of internal alkenes takes place much more slowly.

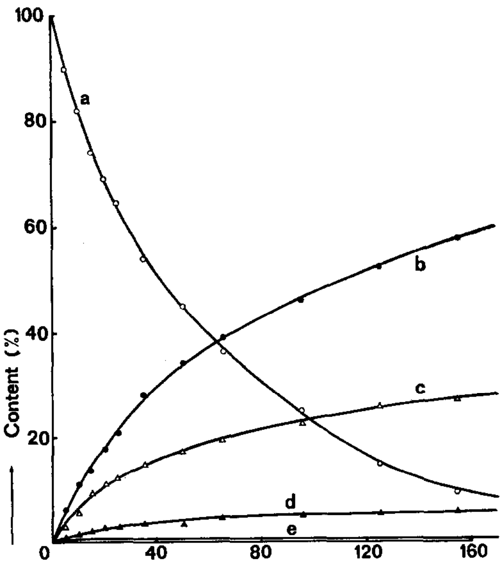

FIG. 1. Hydrogenation at 20°C and 1 atm H_2 of 1-hexene (10 ml) in glacial acetic acid (120 ml) using 250 mg $H_2PtCl_6 \cdot 6H_2O$ (4×10^{-3} *M*) and 600 mg $SnCl_2 \cdot 2H_2O$ (2×10^{-3} *M*); ratio Sn/Pt:5. (a) 1-Hexene; (b) hexane; (c) 2-*trans*-hexene; (d) 3-*trans*-hexene; (e) 2-*cis*- + 3-*cis*-hexene.

Figure 2 represents the results of an experiment in which by application of a higher catalyst concentration, the hydrogen transport has become rate-determining in the hydrogenation; here 1-hexene disap-

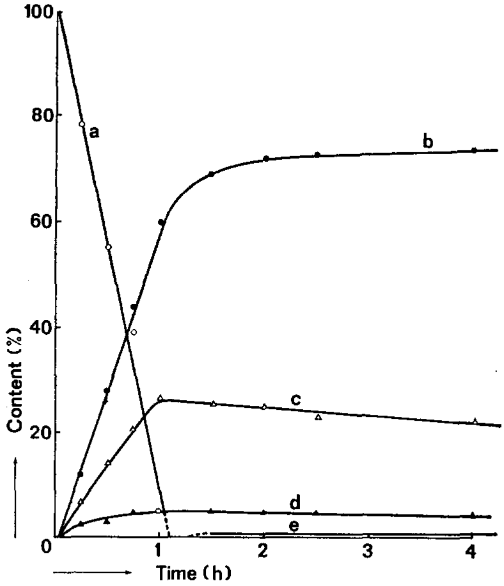

FIG. 2. Hydrogenation at 20°C and 1 atm H_2 of 1-hexene (20 ml) in glacial acetic acid (240 ml) using 1000 mg $H_2PtCl_6 \cdot 6H_2O$ ($8 \times 10^{-3} M$) and 2400 mg $SnCl_2 \cdot 2H_2O$ ($4 \times 10^{-3} M$). (a) 1-Hexene; (b) hexane; (c) 2-*trans*- + 3-*trans*-hexene; (d) 2-*cis*-hexene; (e) 3-*cis*-hexene.

pears according to a pseudo-zero-order reaction. After disappearance of the 1-hexene, the rate of hydrogenation strongly decreases as a result of the slower hydrogenation of the internal alkenes. That the hydrogenation of internal alkenes proceeds so slowly may be attributed to steric effects which have an unfavorable influence on the formation of an alkene-catalyst complex.

In the present investigation, the following variables have been examined:

Reaction temperature: The rate of hydrogenation increases with increasing reaction temperature. At temperatures higher than 80°C, the complex is no longer stable and metallic platinum precipitates.

Substrate concentration: At high substrate concentrations ($>1.25 M$ 1-hexene), the rate of hydrogenation decreases.

Catalyst concentration: For high catalyst concentrations under the conditions applied, the hydrogen transport becomes rate-determining. The same effect can be achieved by lowering the stirring intensity.

Ratio Sn/Pt: At a ratio $Sn/Pt \leq 3$, metallic platinum precipitates. At a ratio $Sn/Pt > 7$, the rate of hydrogenation gradually decreases.

As already found in an investigation carried out by Van Bekkum (*6*) with another system, the addition of salts, such as NaCl and NaBr, to the catalyst system increases the rate of hydrogenation. The effect of bromide is greater than that of chloride.

Apart from alkenes, also unsaturated

TABLE 1

HYDROGENATION[a] OF SOYABEAN OIL USING $H_2PtCl_6 \cdot 6H_2O$ AND $SnCl_2 \cdot 2H_2O$

Time (hr)	n_D^{65}	Melting point (°C)	Iodine value	Trans content (%)	Fatty acid composition (GLC)[b]				
					C 18:0	C 18:1	C 18:2	Iso-C 18:2	C 18:3
0[c]	1.4582	<0	133	0	4.5	22.0	57.5	—	5.0
0.5	1.4577	<0	121	11	5.0	33.5	45.0	—	5.0
1	1.4571	<0	113	19	5.0	40.5	39.0	—	4.5
2	1.4559	16	101.5	33	5.0	51.5	26.5	—	5.0
4	1.4542	23	88	41	4.5	65.5	13.0	—	5.5
6	1.4533	28	81	49	5.0	72.5	6.0	—	4.0
8	1.4523	30	78	55	5.0	79.0	1.5	—	3.0
10	1.4521	31	75.5	57	4.5	80.5	2.0	1.0	tr
12	1.4520	32	75.7	60	5.5	79.5	2.0	1.0	tr
15	1.4518	33	74.7	60	5.5	79.0	2.0	1.5	tr

[a] Temperature, 40°C; 1 atm H_2; 50 ml soyabean oil in 240 ml acetic acid; 1000 mg $H_2PtCl_6 \cdot 6H_2O$ and 2400 mg $SnCl_2 \cdot 2H_2O$.

[b] Invariably present about 12% C 16:0.

[c] Starting material.

edible oils can be hydrogenated with the above mentioned catalyst system. Table 1 represents the hydrogenation of soyabean oil using acetic acid as solvent. Here, the catalyst system has a remarkable preference for the hydrogenation of linoleic acid. As long as some linoleate is present, hardly any linolenate is hydrogenated. In addition, the catalyst has a considerable selectivity for the formation of oleate. As appears from the trans content, isomerization of the double bonds also takes place here. Methyl esters from soyabean oil give more or less the same picture.

As solvents, the fatty acid homologs from acetic acid to stearic acid inclusive have been investigated. In all cases the catalyst was active. Other suitable solvents are ketones such as acetone, methyl ethyl ketone, and diethyl ketone, as well as a number of ethers such as diethyl ether, and dipropyl ether, tetrahydrofuran, and nitrobenzene.

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Received December 13, 1966

Kinetics of the Low Pressure Nitrous Oxide Decomposition on Iridium and Palladium Filaments

INTRODUCTION

The catalytic decomposition of nitrous oxide has been investigated on various metals and metal oxides (*1*, *2*). In this paper, the decomposition kinetics on iridium and palladium are reported.

EXPERIMENTAL

Apparatus. The experimental setup is the same as that previously described in ref. (*2*). Essentially, it consists of a gas-handling system for purification and storage of gases and a reactor flask in which the filament is mounted. The reactor is connected to a mass spectrometer which in turn monitors the reaction. The apparatus is given a modest bake-out (250°C) before a run while Vac-ion pumping is used to reduce the pressure in the system to at least 10^{-8} torr. A mass spectrometer is directly connected to the reactor through a by-pass valve to detect leaks and analyze gases desorbed from the filament when it is flashed before a run.

Materials. The gases (N_2O, N_2, and O_2) were commercially available and purified by freezing out the impurities in liquid nitrogen or Dry Ice cold traps.

The calculated surface areas of the filaments are given in the tables; they are in the range of 1 cm^2.

RESULTS

1. Iridium Filaments

a. Decomposition kinetics. The decomposition on iridium has been found to fit the following rate equation: