JOURNAL OF CATALYSIS **27**, 452–477 (1972)

NOTES

Hydrogenation of Cyclohexene Catalyzed by Solutions of Hydridocarbonyltris(triphenylphosphine)rhodium(I)

O'Connor and Wilkinson (*1*) have shown that hydridocarbonyltris(triphenylphosphine)rhodium(I) is an efficient and highly selective catalyst for the hydrogenation of alk-1-enes. There was no detectable hydrogenation with alk-2-enes and cyclohexene. We have now studied the hydrogenation of cyclohexene under elevated pressures and at a temperature slightly higher than that used by O'Connor and Wilkinson (*1*), and we have shown that under these conditions it has been possible to achieve a complete hydrogenation of cyclohexene to cyclohexane.

Cyclohexene BDH (>99%) was purified by distillation, kept over sodium and filtered through a layer of alumina (chromatography grade, Merck activity 0). Benzene (Riedel de Haën, A. R. for chromatography) was dried over sodium. Hydridocarbonyltris(triphenylphosphine)rhodium(I) was prepared according to Evans *et al.* (*2*). The complex was identified by measuring the M–H and the carbonyl stretching frequency on a Perkin Elmer Model 700 IR-spectrophotometer. The catalyst was dried in vacuum.

The experiments were conducted in a stainless steel high-pressure 500-ml reactor (Ingenieurbureau SFS Zürich) fitted with a stirrer magnetically coupled to an electric motor and operated at 1000 rpm. Above that speed no acceleration of the reaction was observed. The temperature of the reaction mixture was kept constant by circulating oil through the reactor jacket from a thermostat and was automatically recorded.

The complex solution in benzene was placed in the reactor, which was purged several times with hydrogen and held under a hydrogen pressure of 60 atm. for 16 hr in order to insure that no dimeric complex $[Rh(CO)(PPh_3)_2]_2$, as reported by Yagupsky *et al.* (*3*) was present. After 16 hr the hydrogen pressure was lowered to 10 atm. and the solution of cyclohexene in benzene was injected into the reactor. All experiments were carried through with 0.5 mol/liter as the initial concentration of cyclohexene. The pressure was adjusted to the required value, the temperature to 50°C, and the stirrer turned on. The measurements of hydrogen absorption were carried out by following the pressure change by means of a pressure transducer and a recorder. After the termination of the reaction the mixture was analyzed by liquid vapor chromatography for cyclohexane and cyclohexene.

The rate of hydrogenation of cyclohexene was found to depend on the concentration of the catalyst. The initial rates of reaction are plotted against the complex concentration in Fig. 1. A definite maximum was observed. Above a complex concentration of about 7.5×10^{-4} mol/liter only traces of cyclohexane were formed. At lower complex concentrations practically all the cyclohexene was hydrogenated to cyclohexane. The rate of hydrogenation of hexene-1 as reported earlier (*1*) was linearly proportional to the complex concentration over a wide range.

O'Connor and Wilkinson (*1*) stated that at concentrations of the complex below 4 ×

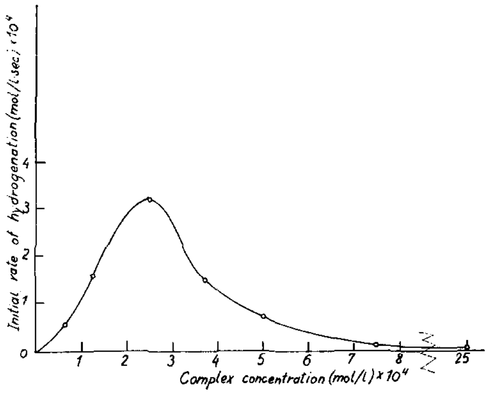

FIG. 1. Initial rate of reaction for hydrogenation of cyclohexene versus complex concentration at fixed temperature (50°C) and hydrogen pressure (30 atm).

10^{-4} mol/liter dissociation [according to the equation $RhH(CO)(PPh_3)_2 \rightleftarrows RhH(CO)(PPh_3) + PPh_3$] becomes important and that $RhH(CO)(PPh_3)$ should be a more active but less selective catalyst than $RhH(CO)(PPh_3)_2$. An increase of the total concentration of the Rh-complex will decrease the relative concentration of $RhH(CO)(PPh_3)$, but the absolute concentration of $RhH(CO)(PPh_3)$ can never decrease by increasing the total concentration of the Rh-complex.

Supposing that $RhH(CO)(PPh_3)$ is the only active catalyst by the hydrogenation of cyclohexene, one should expect the rate to be increased and eventually level off by increasing the total Rh-complex concentration. However, a maximum at an Rh-complex concentration of 2.5×10^{-4} mol/liter and the complete deactivation of the catalytic system at concentrations above 10^{-3} mol/liter cannot be explained by the dissociation.

It is difficult to find a reasonable explanation for this extraordinary behavior, but perhaps it may be due to some sort of interaction of complex molecules.

At a fixed complex concentration of 2.5×10^{-4} mol/liter and a temperature of 50°C the dependence of the rate of hydrogenation on hydrogen pressure was investigated in the range 0–70 atm. The rate of the reaction rose with the pressure, but the increase was not linear and diminished at higher pressures. The reaction order with respect to hydrogen was found by regression analysis to be 0.73 ± 0.09.

REFERENCES

1. O'CONNOR, C., AND WILKINSON, G., *J. Chem. Soc. A*, 2665 (1968).
2. EVANS, D., YAGUPSKY, G., AND WILKINSON, G., *J. Chem. Soc. A*, 2660 (1968).
3. YAGUPSKY, M., BROWN, C. K., YAGUPSKY, G., AND WILKINSON, G., *J. Chem. Soc. A*, 937 (1970).

JES HJORTKJÆR
ZDZISLAW KULICKI

Institutet for Kemiirdustri
DtH
Bygning 227
DK-2800 Lyngby, Denmark
Received January 14, 1972

On the Mechanism of Sulfur Poisoning of Platinum Catalysts

The inhibition of a large variety of surface reactions that are catalyzed by supported platinum particles by a very small amount of sulfur has been well documented (*1*). Estimates based on experimental data indicate that each sulfur atom may render 6 to 10 platinum atoms ineffective for the ring opening of cyclopentanes (*1*), demethylation (*2*) or for other catalytic surface reactions. In chemical reactions that take place in the solid state, a large chemical change that is associated with the presence of small amounts of impurities frequently indicates the onset of phase transformations that are accompanied by marked changes of atomic structure.