

## Liquid Phase Hydrogenation of 1-Hexene and 2-Hexene with 30 Å Platinum Particles on Alumina Support

MAGALI BOUTONNET,<sup>a</sup> CARLAXEL ANDERSSON<sup>b</sup> and RAGNAR LARSSON<sup>b</sup>

<sup>a</sup> Université Louis Pasteur, Institut de Chimie, Strasbourg, France and <sup>b</sup> Inorganic Chemistry 1, Chemical Center, University of Lund, Lund, Sweden

1-Hexene has been hydrogenated in ethanol solution with two different supported platinum catalysts. One had been prepared by reduction of a platinum salt in an inverted micelle and had a very narrow particle size distribution. It was supported on Al<sub>2</sub>O<sub>3</sub>. The other was a commercial Pt/SiO<sub>2</sub> catalyst (EUROPT-1). The activation energies were 21.5 kJ mol<sup>-1</sup> and 37.0 kJ mol<sup>-1</sup>, respectively. *trans*- and *cis*-2-hexene were found to have a somewhat lower rate than that of 1-hexene. For *cis*-2-hexene some *trans*-isomer was formed during the hydrogenation.

The purpose of this investigation has been to test the catalytic properties of platinum particles prepared by the reduction of chloroplatinic acid under the influence of certain surfactant agents. The principle idea for the preparation is that the platinum salt should be incorporated into an inverted micelle. As the volume of the cavity of the micelle is defined one expects a well-defined size of the particles thus produced on reduction. The preparation of the particles used in our work has been described in detail elsewhere.<sup>1</sup> The particle-size distribution curve shows a pronounced maximum at 30 Å, 67% of the particles falling within 28–32 Å and no particles falling outside the limits 25 and 35 Å.

The quantitative kinetic experiments were performed on an ethanolic solution of 1-hexene with the platinum particles supported on aluminium oxide or pumice. Four different ways of preparation of the supported catalysts were tested as indicated in Table 1. Some qualitative experiments were also made on *cis*-2-hexene and *trans*-2-hexene to study the variation of

isomerization reactions. The 1-hexene reaction was also studied for comparison using a commercial Pt/SiO<sub>2</sub> catalyst, Johnson Matthey 6.3% Pt, established as a reference system (EUROPT-1) within the Council of Europe Research Group on Catalysis.

### EXPERIMENTAL

*Materials.* The preparation of the four catalysts is described in Table 1. In all cases the platinum salt is reduced to metal particles with hydrazine hydrate at room temperature before the colloidal solution is applied to the carrier.

The purity of 1-hexene (MERCK) was determined by gas chromatography to 97% with 1.4% *n*-hexane, 1.5% *cis*-2-hexene and traces of low molecular weight hydrocarbons. *cis*-2-Hexene and *trans*-2-hexene were both from FLUKA and of high purity as shown by gas chromatography. The solvent was 99.5% ethanol.

*Procedure.* The apparatus of hydrogenation was essentially the same as used by Schrock and Osborn.<sup>2</sup>

The catalyst was placed in the reaction vessel together with a magnetic teflon-covered stirring bar, the solvent was frozen by liq. nitrogen in a rotatable side flask and the vessel was evacuated. After thawing, the solvent was poured into the main vessel and hydrogen was introduced to a total pressure of 1 atm. The catalyst was then stirred in the solvent under hydrogen for ten min, whereupon the olefin was injected through a serum cap. The total pressure was maintained during the hydrogenation at 1 atm with the aid of a leveling manometer and by periodic addition of hydrogen. The reaction was followed by withdrawing 0.2 μl samples of the reaction mixture at certain intervals.

Table 1. Mode of preparation of the supported catalysts. The following abbreviations are used: Hexadecane = H. Penta-ethyleneglycol dodecylether = PEGDE.

Catalyst	System	Carrier	Conc. of Pt %	Process of deposition
1	H 60 % PEGDE 30 % aq. sol. of $\text{H}_2\text{PtCl}_6$ 8 % ( $1 \times 10^{-3}$ g Pt/g)	$\text{Al}_2\text{O}_3$ high content of surface OH groups (WOEHLM)	2	The colloidal solution was centrifuged and the metal particles were redispersed by ultrasound to an ethanolic solution and the carrier was added. Deposition took place at a slow agitation of the system. The catalyst was dried in a dessicator after washing with ethanol several times.
2	H 90 % PEGDE 10 % ( $3.8 \times 10^{-3}$ g Pt/g)	Pumice	2	The carrier is added directly to the colloidal solution and the pH of the solution is increased by adding hydrazine (pH = 8). Deposition is done by agitation. The resulting catalyst was washed several times with ethanol and dried at 120 °C.
3	H 60 % PEGDE 32 % aq. sol. of $\text{H}_2\text{PtCl}_6$ 8 % ( $12 \times 10^{-3}$ g Pt/g)	$\text{Al}_2\text{O}_3$ neutral (WOEHLM)	2	The same process of deposition as for catalyst 2 was used in this case. The only difference was the use of 1 M NaOH (pH = 11) instead of hydrazine.
4	<i>n</i> -hexan 91.2 % PEGDE with $\text{H}_2\text{PtCl}_6$ 8.8 % ( $3.3 \times 10^{-3}$ g Pt/g)	$\text{Al}_2\text{O}_3$ neutral (WOEHLM)	1.1	The colloidal solution was applied step by step on the alumina and the solvent was eliminated by filtration. The catalyst was washed with ethanol and dried under vacuum.

The products were analyzed by GLC with a 1.5 m  $\times$  2.3 mm (I.D.) column packed with DURAPAK *n*-octane/porasil C. 100/120 mesh. The carrier gas, nitrogen, had a flow rate of 35 ml/min. The temperature of the column was 40 °C, maintained by a cooling system with carbon dioxide gas. The temperature of the detector was 375 °C and of the injector 100 °C.

## RESULTS

*Hydrogenation of 1-hexene.* The extent of the reaction ( $\xi$ ), expressed as the amount formed of *n*-hexane, was in most cases proportional to the time elapsed (Fig. 1a). This means that the reaction is of zero order with respect to olefin, a situation often met in olefin hydrogenation.<sup>3</sup>

The rate was assumed to be directly proportional to the hydrogen pressure as reported by Ualikhanova *et al.*<sup>4</sup> This assumption is also

applied in extensive investigations by Ruzicka *et al.*<sup>5</sup> Hence it is possible to express the rate constant in  $\text{mol atm}^{-1} \text{s}^{-1} \text{g}_{\text{Pt}}^{-1}$  (Table 2). The hydrogen pressures reported in Table 2 were calculated for each temperature using tabulated data<sup>6</sup> of vapour pressures of ethanol and 1-hexene and assuming, in want of better information, the vapour pressure to be directly proportional to the mol fraction.

Only in some cases – at the highest temperatures – a curved line described *c versus* time, *i.e.* the olefin order was in most cases 0. The “rates” given in Table 2 for these systems are rough mean values of the slope of what appeared to be a first linear portion of the curve (Fig. 1b). Close examination of the curve showed, however, that the limiting slope at  $t=0$  was actually larger than thus reported. Unfortunately, the data did not allow an accurate extrapolation to be done, but one should bear in mind when considering the curvature of the

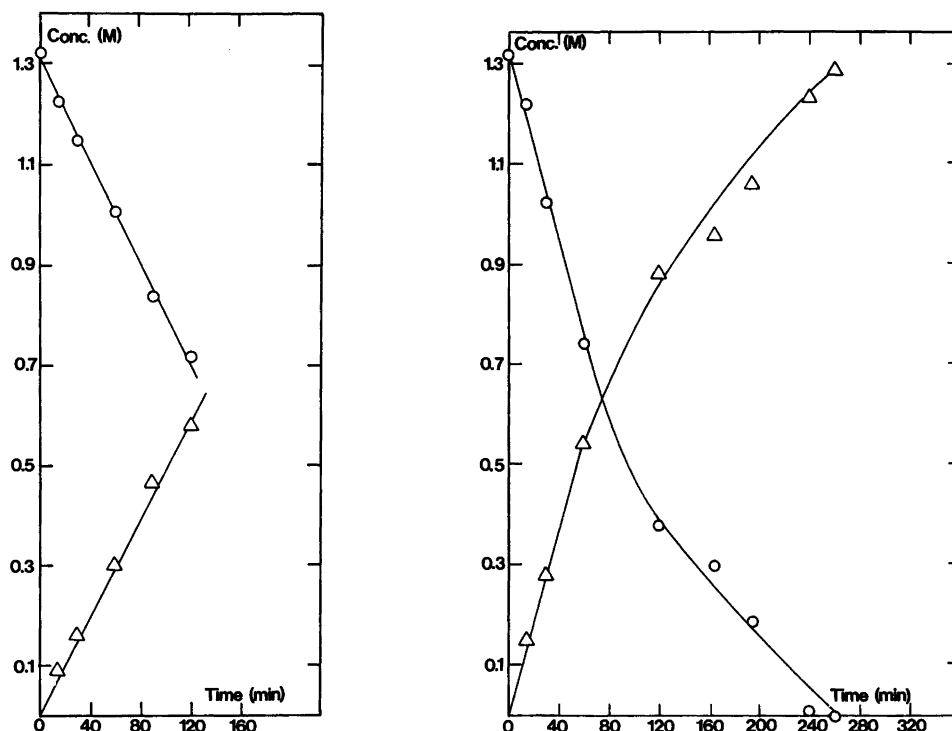


Fig. 1. Representative examples of the course of reaction. The concentrations of hexane formed ( $\Delta$ ) and 1-hexene remaining ( $\circ$ ) are plotted against time. As the volume was 6 ml one easily gets the amount of hexane, i.e. the extent of the reaction. The limiting slope of the curve gives  $d\xi/dt$  as reported in Table 2. a. Experiment f, i.e. catalyst No. 3 and temperature  $+2^\circ\text{C}$ . b. Experiment d, i.e. catalyst No. 3 and temperature  $+30^\circ\text{C}$ .

Arrhenius diagrams (Fig. 2) that the points for the highest temperatures could be somewhat low.

Most experiments were performed on the  $\text{Al}_2\text{O}_3$  (neutral) supported catalyst and for this system the results are given in an Arrhenius plot (Fig. 2). One observes that for the high temperatures a deviation from the straight line occurs. This effect is often met in heterogeneous catalysis<sup>7</sup> and can have two reasons: (a) The reaction is diffusion controlled, or (b) The adsorption coefficient is small and the enthalpy of adsorption is comparable to the value of the activation energy.

It is not obvious which of these effects apply here. However, if the reaction was diffusion controlled one would expect less than proportionality of the rate to the amount of catalyst, *cf.*, *e.g.* Ref. 7. Experiment h, Table 2, with twice the amount of Pt, shows that a rough proportionality holds (compare

exp. d). Therefore we suggest that the last alternative is the relevant one and that the straight line for the low temperature points describes the true activation energy.

As indicated above, two other factors might influence the direction of the curve at the highest temperatures, the deviation from ideal adherence to Raoult's law and the possible non-zero order of the reaction with respect to olefin. The decline of the slope should, therefore, not be discussed in too great detail.

Some experiments were also performed with catalyst No. 4. No essentially different behaviour was found for this system. Thus it appears that neither the nature of the support nor the small variations of preparation of the colloidal Pt particles influence the catalytical pattern very much.

In Table 2 we have also included the results

Table 2. Rates of reaction and rate constants for the hydrogenation of 1-hexene ( $P_{\text{tot}} = 1$  atm). Volume of the liquid phase was 6 ml unless otherwise stated.

Exp.	Catalyst	Temp. °C	$\frac{10^3}{T}$ (K)	$p_{\text{H}_2}$ (atm)	Rate $d\xi/dt$ $\text{mmol min}^{-1}$	$w_{\text{Pt}}$ mg	$k_m$ $\text{mol atm}^{-1}$ $\text{s}^{-1} \text{g}_{\text{Pt}}^{-1}$	$k_a 10^4$ $\text{mol atm}^{-1}$ $\text{s}^{-1} \text{m}^{-2}$	$\log k_a + 4$
a	No. 1	30	3.30	0.89	6.05	0.5	0.227	24.4	1.39
b	No. 2	30	3.30	0.89	5.75	0.5	0.215	23.1	1.36
c	No. 3	50	3.10	0.72	5.75	0.5	0.266	28.5	1.45
d		30	3.30	0.89	5.41	0.5	0.203	21.8	1.34
e		13	3.49	0.96	4.38	0.5	0.152	16.3	1.21
f		2	3.64	0.98	2.95	0.5	0.100	10.7	1.03
g		-10	3.80	0.99	1.99	0.5	0.067	7.2	0.86
h	No. 3	30		0.89	12.5	1.0	0.468		
i	EuroPt	50	3.10	0.72	15.5	0.5	0.717	47.4	1.68
j		30	3.30	0.89	12.8	0.5	0.479	31.7	1.50
k		14	3.48	0.95	9.2	0.5	0.323	21.3	1.33
l		1	3.65	0.98	5.0	0.5	0.170	11.2	1.05
m		-4	3.72	0.99	3.90	0.5	0.131	8.7	0.94
n		-14	3.86	0.99	1.99	0.5	0.067	4.4	0.65
o		50		0.72	5.6	1.0	(Volume = 12ml)		

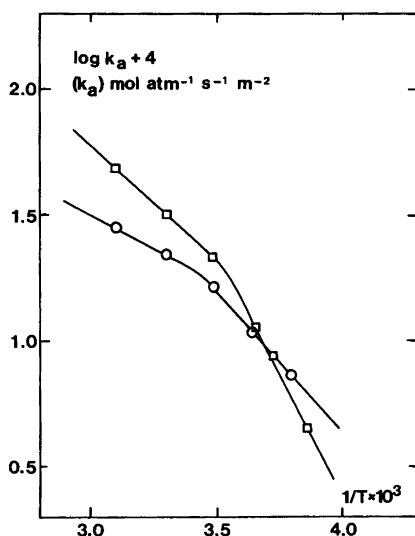


Fig. 2. Arrhenius diagram for the areal rate constants ( $k_a$ ).  $\circ$  denotes the 30 Å Pt-catalyst and  $\square$  denotes the EUROPT catalyst.

reached using the EUROPT-1 catalyst. The same pattern of effects appears also for this system. In one experiment with this catalyst we doubled the amount of catalyst as well as the volume of the reaction mixture (Exp. o, Table 2). As all other parameters, including the hydrogen pressure and stirring device, were unaltered this experiment can be regarded as a test for a possible diffusion control of the reaction. Actually, we found that the rate was decreased, indicating that the supply of hydrogen was not rapid enough to sustain the increased consumption following the increase of platinum and substrate. This is probably caused by the too heavy load on our stirring device which was optimized for the small volume of the reaction mixture normally used (*cf.* Ref. 7 p. 82). However, the rates caused by the EUROPT-1 catalyst were generally higher than those caused by the 30 Å Pt catalysts.

As no rates for the 30 Å catalyst experiments are higher than  $6 \text{ mmol min}^{-1}$  we have used only rates below this value to establish the straight line of the EUROPT-1 experiments, too. Hence both values calculated for the activation energies apply to

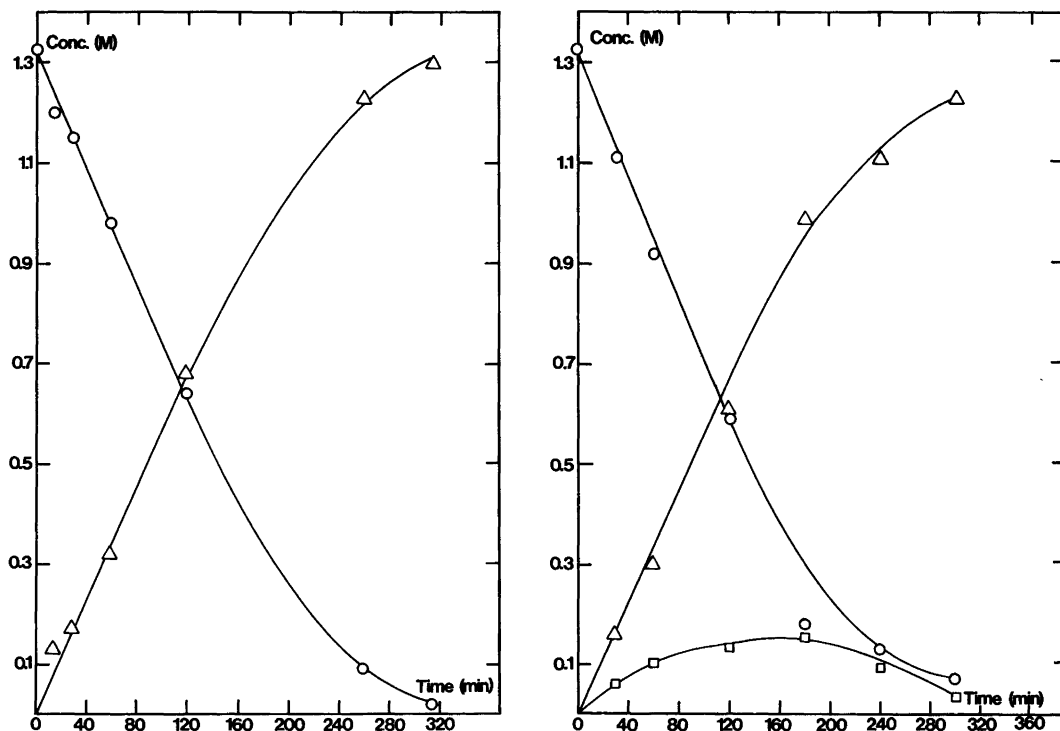


Fig. 3. Hydrogenation of 2-hexene (25 mg catalyst No. 3, corresponding to 0.5 mg Pt). a. *trans*-2-Hexene  $\square$ . b. *cis*-2-Hexene  $\circ$ . In both figures  $\triangle$  denotes hexane.

experiments where the rate is not diffusion controlled.

The activation energies are  $21.5 \pm 1 \text{ kJ mol}^{-1}$  for the 30 Å catalyst and  $37.0 \pm 1 \text{ kJ mol}^{-1}$  for the EUROPT-1 catalyst. Although these figures might be regarded as surprisingly low, such values of activation energies are actually often met for the heterogeneous hydrogenation of olefins.<sup>3</sup> When more data are collected for well characterized metal particle systems it might be possible to discuss the values in relation to the structure and properties of the particles.

As we know the mean particle size for both the catalysts studied<sup>1,8</sup> (30 and 18.5 Å, respectively), it is possible to express the area rate,  $r_a$ , and the corresponding rate constants,  $k_a$ . We have assumed the particles to have half-spherical shape, giving an area of  $93 \text{ m}^2 \text{ g}_{\text{Pt}}^{-1}$  for the 30 Å catalyst and  $151 \text{ m}^2 \text{ g}_{\text{Pt}}^{-1}$  for the EUROPT-1.

From this we arrive at the values reported in the last column of Table 2. They are plotted in Fig. 2 to

emphasize the similarity of the rates of the two catalytic systems and the difference of activation energies.

*Hydrogenation of 2-hexene.* Using the catalyst No. 3 (Table 1) we performed the measurements that are reported in Figs. 3a and 3b. The *trans*-2-hexene isomer (Fig. 3a) behaved very similarly to 1-hexene. The rate, at 30 °C, was found to be  $3.4 \text{ mmol min}^{-1}$ , i.e. somewhat lower than found for 1-hexene at the same temperature (Table 2). Also the rate for *cis*-2-hexene (expressed in the amount of hexene formed) was found to be  $3.3 \text{ mmol min}^{-1}$ . In this case the appearance of *trans*-2-hexene was noticeable (Fig. 3b). At most, the concentration of the *trans*-isomer was 10% of the total concentration of hydrocarbons.

The very similar rate of hydrogenation indicates a rapid transformation of the *cis*-isomer to the *trans* one, followed by the hydrogenation of the latter. This is expected as the *trans*-isomer is the more stable one from a thermodynamical point of view.

(Also in the experiments on 1-hexene some amount of *trans*-2-hexene was found. It was not more than a few percent, however.)

*Acknowledgements.* This work was supported by *Styrelsen för Teknisk Utveckling* (The Swedish Board for Technical Development). One of us (M.B.) wants to thank Prof. Per Stenius for providing working facilities during her stay in Stockholm.

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Received April 18, 1980.