

## THE EFFECT OF SOLVENTS ON THE COURSE OF HYDROGENATION OF 1-PHENYL-2-PROPENE AND 4-NITROTOLUENE ON A PLATINUM CATALYST\*

L. ČERVENÝ and V. RŮŽIČKA

*Department of Organic Technology,  
Prague Institute of Chemical Technology, 166 28 Prague 6*

Received September 10th, 1975

Hydrogenation of 1-phenyl-2-propene and 4-nitrotoluene on a catalyst containing 5% platinum on silica gel was performed in a series of seven solvents at normal conditions. Both the individual substrates and their equimolar mixture were hydrogenated. Reaction rates in individual solvents were measured and the course of the competitive hydrogenation was investigated. The effects of solvents on the hydrogenation rate of both substrates and on selectivity of their hydrogenation in the equimolar mixture were tested.

This work is a continuation of preceding studies<sup>1-4</sup>, in which an attempt had been made to express quantitatively the effect of solvents on the course of hydrogenation of olefinic substrates. It had been shown that the effect of solvents on rate and relative adsorption constants may be quantified in series of similar substrates. It was the aim of this work to verify whether it is possible to affect the selectivity of hydrogenation of two different functional groups by the choice of solvent.

### EXPERIMENTAL

*Materials used.* A catalyst containing 5% Pt on silica gel was prepared<sup>5</sup> similarly as in the preceding work<sup>1</sup>. The fraction of mesh size below 0.063 mm was used in the experiments. Commercial 1-phenyl-2-propene (Koch-Light, London) and 4-nitrotoluene (Spolek pro chemickou a hutní výrobu, Ústí nad Labem) were employed as substrates and they were further purified by rectification resp. crystallization from ethanol. Of the original series of nineteen solvents<sup>1</sup>, cyclohexane, diethyl ether, toluene, methanol, benzene, ethyl acetate and 1,4-dioxane had been selected. Their purification and purification of hydrogen had been described earlier<sup>1</sup>. Both hydrogenated substances and all the solvents were chromatographically pure.

*Apparatus and technique* had been described earlier<sup>1-3</sup>. The hydrogenations were performed in an agitated reactor at 20°C and atmospheric pressure of hydrogen. Hydrogenations of individual substances were made with 1 ml of 1-phenyl-2-propene resp. 5 mmol (0.685 g) of 4-nitrotoluene, those of binary mixtures with a solution of 1 ml of 4-nitrotoluene and an equimolar amount

\* Part XL in the series Study of Hydrogenation in the Liquid Phase; Part XXXIX: Sb. Vys. Šk. Chemicko-Technol., Praha, in press.

of 1-phenyl-2-propene in 25 ml of solvent, catalyst amounts were in the range 0.1–0.2 g according to hydrogenation rates in individual solvents. During the reaction, samples of the volume of 0.1 ml were being withdrawn at appropriate time intervals for chromatographic analysis. Volumetrically determined individual rates were corrected to the partial pressure of hydrogen of 98.067kPa (1 at) taking into account the solvent vapour pressure and assuming a first order of the reaction with respect to concentration of hydrogen<sup>1</sup>; these values were then recalculated to unit amount of the catalyst.

*Chromatographic analyses* of reaction mixtures were performed on a Chrom-2 apparatus with flame-ionization detection at 130°C. A glass 2.5 m-long column of 2.5 mm I.D. was employed; it was packed with Chromaton NAW containing 10% of a SE-31 silicon elastomer.

## RESULTS AND DISCUSSION

The kinetic measurements were performed at conditions where the reaction rate was not affected by mass transfer<sup>1,3</sup>. Values of measured reaction rates, which are equal to rate constants in the case of the zeroth order with respect to the reacting substrate, are given Table I. No simple linear relationship could be found between hydrogenation rate constants of both model substrates in our series of solvents. Hydrogenation rates of both substrates in the same solvent are comparable, similarly as those of each of the substrates in the entire series of solvents (lower hydrogenation rates of both substrates in 1,4-dioxane form rather an exception).

It was found by the method of competitive reactions that in the equimolar mixture the hydrogenation of 1-phenyl-2-propene is preferred and the hydrogenation of 4-nitrotoluene starts only after its disappearance from the reaction mixture. As rate constants of both substrates are comparable, this result must be ascribed to a considerable difference in their adsorptivities, resp. adsorptivities of both functional groups.

TABLE I  
Hydrogenation Rates of 1-Phenyl-2-propene (B) and 4-Nitrotoluene (A) in the Series of Solvents

No	Solvent	Hydrogenation rate, ml H <sub>2</sub> /min g <sub>cat</sub>	
		A	B
2	cyclohexane	90.0	13.18
4	diethyl ether	49.2	42.40
10	toluene	40.1	52.60
11	methanol	75.6	81.25
12	benzene	55.5	14.85
13	ethyl acetate	10.5	57.95
15	1,4-dioxane	6.2	1.80

Table II comprises selectivity factors  $S_{A,B}$  for which it holds<sup>6</sup>

$$S_{A,B} = (k_A/k_B) K_{A,B} \quad (1)$$

for different actual compositions of the reaction mixture expressed in actual concentrations of components A and B related to their initial concentrations. If, at a 99% degree of conversion of component B, the degree of conversion of component A reaches 1% (which is observable by the given method of analysis), the value of the selectivity factor leads to the value of the relative adsorption coefficient  $K_{A,B} = 2.18 \cdot 10^{-3}$  at comparable values of the rate constants  $k_A$  and  $k_B$ . The adsorption coefficient of 1-phenyl-2-propene is therefore at least 460 times higher than that of 4-nitrotoluene. It may be expected that its actual value is still much higher, however, it cannot be determined by the method of competitive reactions.

Although a change of the solvent may affect both the rate and relative adsorption constants<sup>4</sup> in the olefinic series as well as in the series of aromatic nitro compounds<sup>7</sup>, this change does not lead to a change of the selectivity during the competitive hydrogenation of 1-phenyl-2-propene and 4-nitrotoluene. This fact is obviously brought about by substantially higher adsorptivity of the double bond on the employed platinum catalyst in comparison with the nitro group in all the examined solvents.

TABLE II

Selectivity Factors  $S_{A,B}$  for Different Actual Compositions of the Mixture of Components A and B during Competitive Hydrogenation of Their Equimolar Mixture

Compositions of the reaction mixture in relative concentrations		Selectivity factor $S_{A,B} \cdot 10^3$
$C_A$	$C_B$	
0.99	0.01	2.18
0.98	0.02	4.87
0.97	0.03	8.69
0.96	0.04	12.68
0.95	0.05	17.12
0.90	0.10	45.67
0.80	0.20	138.65
0.70	0.30	296.24
0.60	0.40	557.50
0.50	0.50	1 000.00

## REFERENCES

1. Červený L., Červená J., Růžička V.: This Journal 37, 2946 (1972).
2. Červený L., Procházka A., Železný M., Růžička V.: This Journal 38, 3134 (1973).
3. Červený L., Procházka A., Růžička V.: This Journal 39, 2463 (1974).
4. Červený L., Urbanová E., Růžička V.: This Journal 40, 3659 (1975).
5. Pines H., Obberg R. L., Ipatieff V. N.: J. Amer. Chem. Soc. 70, 533 (1948).
6. Rader Ch. P., Smith H. A.: J. Amer. Chem. Soc. 84, 1443 (1962).
7. Červený L., Bartoň J., Růžička V.: Unpublished results.

Translated by K. Hlavatý.