COMPETITIVE HYDROGENATION OF A PAIR OF SUBSTRATES IN COMBINED TWO-CATALYST SYSTEMS

Libor ČERVENÝ, Barbora VODOVÁ and Vlastimil RŮŽIČKA

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

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A theoretical model has been set up for treating competitive hydrogenations of pairs of substrates on combined two-catalyst systems, assuming that the catalysts act in an independent manner. The hydrogenation rate constants of the two substrates and their relative adsorptitives established on the individual catalysts are used for the calculations. The model has been tested on the substrate system of 2-methyl-3-buten-2-ol and 2-phenylpropene, hydrogenated in methanol or cyclohexane on combined Pt/C, Pd/C, and Rh/C catalyst systems. The calculated and observed data are in a good agreement.

In systems where two substrates are competitively hydrogenated on two catalysts, two ways of catalyst action are conceivable: either the catalyst action is synergistic, which, however, for hydrogenations of the same functional groups on a mechanical mixture of catalysts is highly improbable; or the catalysts act in an independent manner, the kinetics of the reactions on them being, however, mutually related through the concentration changes brought about by the effect of both catalysts. In the latter case the selectivity of the competitive hydrogenation will lie between the values corresponding to the individual catalysts. A treatment of such systems is the objective of the present work.

Consider the simplest kinetics, which for substance A from the pair A, B is expressed by

$$r_A = k_A K_A C_A/(1 + K_A C_A)\,, \tag{1}$$

where r_A is the reaction rate, k_A is the corresponding rate constant of the surface reaction, K_A is the adsorptivity of the substance, and C_A is its concentration.

The kinetic constants of hydrogenation of substances A and B, k_A and k_B, can readily be determined in the zeroth order region ($K_A C_A \gg 1$). From the individual measurements, knowing the k_A and k_B values, the so-called relative adsorptivity $K_{A,B} = K_A/K_B$ can be determined based on the Rader–Smith relation[1] for competitive hydrogenations,

$$S_{A,B} = r_A/r_B = k_A K_A C_A/k_B K_B C_B\,. \tag{2}$$

Systems involving two catalysts in which a pair of substrates is competitively hydrogenated can be treated in terms of the data obtained for either catalyst separately. Let the subscripts 1 and 2 refer to the two catalysts, respectively. By definition,

$$(S_{A,B})_i = (k_A K_A)_i/(k_B K_B)_i \quad (i = 1, 2)\,. \qquad (3a, b)$$

In a system where the competitive hydrogenation of substances A and B proceed on catalysts 1 and 2, the overall selectivity will be defined as

$$S_{A,B} = r_A/r_B = \{G_1[k_A K_A C_A/(1 + K_A C_A + K_B C_B)]_1 + G_2[k_A K_A C_A/(1 + K_A C_A + K_B C_B)]_2\}/\{G_1[k_B K_B C_B/(1 + K_A C_A + K_B C_B)]_1 + G_2[k_B K_B C_B/(1 + K_A C_A + K_B C_B)]_2\}\,, \qquad (4)$$

where G_1 and G_2 are the mass amounts of the two catalysts employed; hence, in the system of two catalysts the selectivity is far from a simple function of the concentrations as it is for a system with a single catalyst.

Eq. (*4*) is difficult to solve; the solution would require the use of numerical methods. For practical purposes, however, it is convenient *a*) to neglect the unity in the adsorption terms, which is reasonable in view of the fact that during liquid phase hydrogenations of olefinic substrates the catalyst surface is always occupied completely[2] by substances A and B, and *b*) to consider the situation where the selectivity is unity, hence, a system where during the entire competitive hydrogenation of an equimolar mixture of substances A and B the ratio of their instantaneous concentrations remains constant. In this manner, Eq. (*4*) simplifies considerably.

Combining Eqs (*3a*, *b*) with the simplified form of Eq. (*4*) we arrive at the relation

$$G_1/G_2 = [(S_2 - 1)/(1 - S_1)]\,[(k_B)_2/(k_B)_1]\,[K_A/K_B)_1 + 1]/[(K_A/K_B)_2 + 1]\,. \qquad (5)$$

Thus, knowing the values obtainable from experiments with the individual catalysts, *i.e.*, the rate constants, relative adsorptivities, and selectivities of the competitive hydrogenation, the ratio of the mass amounts of the catalysts G_1/G_2 can be calculated such that the selectivity of the competitive hydrogenation on them will be unity.

EXPERIMENTAL

Substances. 2-Methyl-3-buten-2-ol(Koch-Light) and 2-phenylpropene (Lachema, Brno) were commercial chemicals and were freshly distilled prior to use. Methanol and cyclohexane were of reagent grade purity (both Lachema, Brno). The catalysts were 2·8% Pd/C (Cherox 4100, Chemical Works, Záluží), and 5%Pt/C and 5% Rh/C prepared after[3,4] on Supersorbon Degussa HB-3 activated carbon; all of them were used in powder form, the grain size was below 0·063 mm.

Apparatus and procedure. The hydrogenations were carried out at 20°C and atmospheric pressure in a conventional apparatus[5]. 10 ml of solvent was used with 1 ml of an equimolar mixture of 2-methyl-3-buten-2-ol and 2-phenylpropene (or 1 ml of a single substrate), the catalysts were jaken in amounts of 5—100 mg. For the reaction course monitoring, samples were taken and subtected to chromatographic analysis.

Analytical methods. The analyses were performed on a Chrom 4 instrument with flame ionization detection using a glass column 3·5 m × 2·5 mm i.d. packed with 15% SE-31 on Chromaton NAW-DMCS, grain size 0·16—0·20 mm, at 110°C.

RESULTS AND DISCUSSION

The theoretical relations were tested using 2-methyl-3-buten-2-ol as substance A and 2-phenylpropene as substance B; methanol and cyclohexane served as solvents. The measurements were accomplished in conditions in which the effect of mass transport on the hydrogenation course was eliminated[6]. The hydrogenation rates of the substrates were zeroth order up to high degrees of conversion. The corresponding reaction constants k_A and k_B, in ml H_2/min g_{cat}, are given in Table I for the three catalysts used. Except in the hydrogenation on the Rh catalyst in methanol, 2-methyl-3-buten-2-ol was invariably more reactive than 2-phenylpropene. The catalyst activity decreased in the order Pd > Pt > Rh, again with the single exception of the relatively high rate of hydrogenation of 2-phenylpropene in methanol on the rhodium catalyst. The hydrogenation of both substrates was faster in methanol than in cyclohexane.

The selectivity of the competitive hydrogenation of the two substrates was determined for the individual catalysts, and the relative adsorptivity was calculated based on the known k_A and k_B values (Table I). While on the Pt and Rh catalysts 2-methyl-

TABLE I

Kinetic parameters of hydrogenations of 2-methyl-3-buten-2-ol (A) and 2-phenylpropene (B) at 20°C

Catalyst	Methanol				Cyclohexane			
	$k_A{}^a$	$k_B{}^a$	K_A/K_B	$S_{A'B}$	$k_A{}^a$	$k_B{}^a$	K_A/K_B	$S_{A'B}$
2·8% Pd/C	445·6	225·7	0·086	0·17	342·9	108·3	0·218	0·69
5% Pt/C	331·4	119·3	0·377	1·05	234·1	77·0	2·990	0·09
5% Rh/C	180·1	331·3	6·623	3·60	47·1	31·7	16·79	25·0

[a] ml H_2/min g_{cat}.

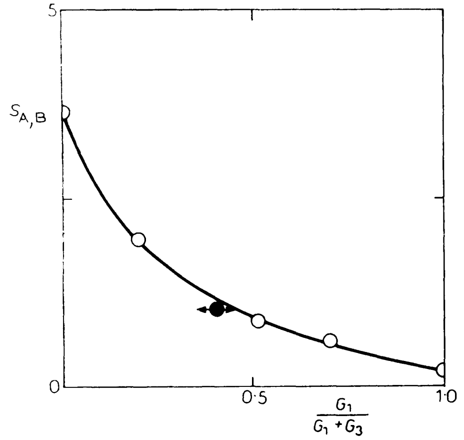

FIG. 1

Dependence of the selectivity of competitive hydrogenation of 2-methyl-3-buten-2-ol (*A*) and 2-phenylpropene (*B*) on the composition of the palladium (*1*) and platinum (*2*) catalyst mixture in methanol

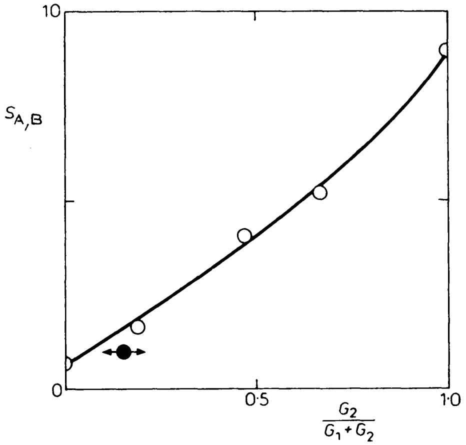

FIG. 2

Dependence of the selectivity of the competitive hydrogenation on the composition of the palladium (*1*) and platinum (*2*) catalyst mixture in cyclohexane

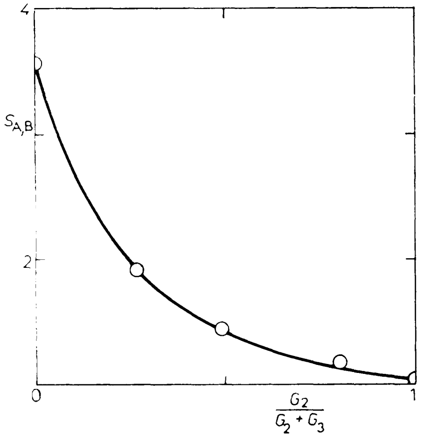

FIG. 3

Dependence of the selectivity of the competitive hydrogenation on the composition of the palladium (*1*) and rhodium (*3*) catalyst mixture in methanol

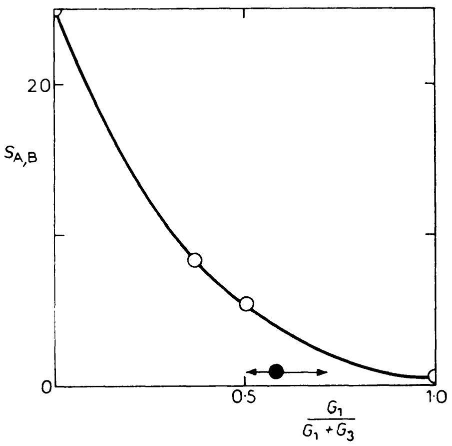

FIG. 4

Dependence of the selectivity of the competitive hydrogenation on the composition of the palladium (*1*) and rhodium (*3*) catalyst mixture in cyclohexane

-3-buten-2-ol was more reactive than 2-phenylpropene in both solvents, the reverse was true of the palladium catalyst. In cyclohexane as solvent the selectivities were multiply higher than in methanol. The difference in the values for the various active metals are difficult to discuss because of lack of complex data[7]. The appreciable increase in the selectivity when passing from methanol to cyclohexane, on the other hand, is consistent with the general concepts[2] of the effects of solvent and of the substrate structure on the hydrogenation. Table I documents that the changes in the selectivity of the competitive hydrogenation are primarily accounted for by the changes in the relative adsorptivity.

The systems with combined catalysts were first tested for synergism. The hydrogenation rates were measured for the individual substrates on all of the catalyst combinations in a mass ratio of 1 : 1 and compared with the arithmetic mean of the rates established on each catalyst separately. The deviations were 0 to 16%, which warrants the statement that in the systems in question the two catalysts involved act in a mutually independent manner. In additional experiments the ratios of the two catalysts in the system was varied; the dependences of the selectivities obtained are shown in Figs 1 – 6. The catalyst mass ratio for which the selectivity should be unity according to Eq. (*5*) is indicated by a full circle. Furthermore, deviations of ±15% from the experimental value were considered for k_A and k_B, and the associated highest

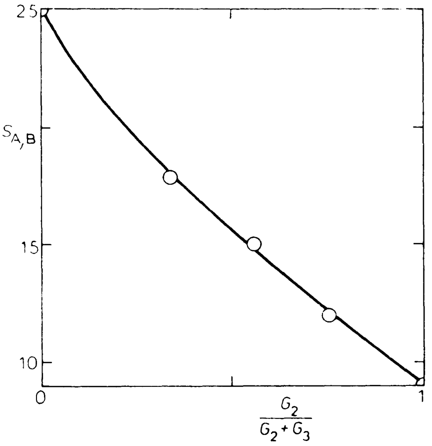

FIG. 5

Dependence of the selectivity of the competitive hydrogenation on the composition of the platinum (*2*) and rhodium (*3*) catalyst mixture in methanol

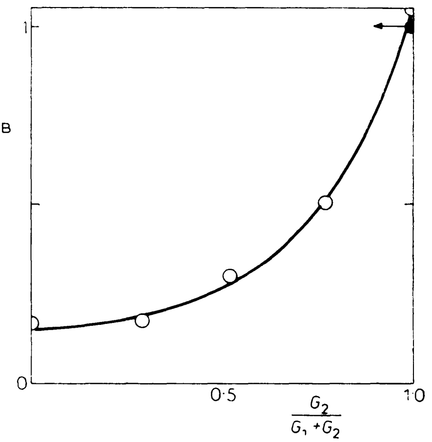

FIG. 6

Dependence of the selectivity of the competitive hydrogenation on the composition of the platinum (*2*) and rhodium(*3*) catalyst mixture in cyclohexane catalyst mass composition deviations from the value to which the selectivity of unity corresponds are the limits of the range indicated by arrows in the figures. The chosen value of $\pm 15\%$ corresponds to the accuracy of measurement; the error in the K_A/K_B ratio depends basically on that in the rate constant values, the measurements of the selectivity being by an order of magnitude more reliable than the reaction rate measurements[7].

The unit selectivity approach is, naturally, inapplicable to systems where the selectivities exceed unity on either catalyst (Pt–Rh); Eq. (*5*) gives a negative mass ratio, lacking physical meaning.

Except for the Pd–Rh catalyst combination in cyclohexane, where the difference in the hydrogenation selectivities is by far the highest, the calculated values fit well the experimental dependences. It can be thus concluded that the results bear out the validity of the theoretical relations for combined competitive hydrogenations, and that the kinetic constant and relative adsorptivity values measured in the one-catalyst systems are reliable enough for their use in the treatment of the combined systems.

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