HYDROGENATION OF 2-PHENYL-1-PROPENE AND 1-HEXENE ON PLATINUM BLACK SURFACE MODIFIED BY Pb, Tl AND Bi ATOMS

Ivo Paseka[a], Libor Červený[b], Dagmar Šmigolová[b] and Vlastimil Růžička[b]

[a] *Institute of Inorganic Chemistry,*
Czechoslovak Academy of Sciences, 169 00 Prague 6 and
[b] *Department of Organic Technology,*
Prague Institute of Chemical Technology, 166 28 Prague 6

Hydrogenation of 2-phenyl-1-propene and 1-hexene in ethanol, toluene and benzene was studied on platinum black modified by ad-atoms of lead, thallium, and bismuth. The experimental dependences of the specific hydrogenation rate on the degree of coverage by the metal ad-atoms are interpreted under the assumptions that the substrate and hydrogen take part in the reaction and at low degrees of the coverage, the organic substance is adsorbed on the modified and non-modified surfaces to the same extent.

The properties of hydrogenation catalysts can be varied to an extent by metals, present on the catalyst surface, which themselves do not adsorb hydrogen. The metals can occur on the surface in the form of a bulk metal phase and in the form of ad-atoms, in dependence on the conditions of the deposition. In hydrogenation reactions these metals more or less lower the catalyst activity[1] and in some cases[2,3] affect also the catalyst selectivity owing to the change in the heat of adsorption of hydrogen. Study of the properties of modified catalysts can contribute to the elucidation of the mechanism of hydrogenation reactions. In the preceding work[4] the hydrogenation rate was studied of 2-phenyl-1-propene on platinum plack modified by copper occurring on the catalyst surface predominantly as a bulk metal phase.

In the present work, the effect has been investigated of ad-atoms of lead, thallium, and bismuth, hence atoms with large atomic radii which in the adsorption block two or three platinum atoms. The study was stimulated also by a recent paper dealing with the effect of Cu, Hg, and Se ad-atoms on the electrochemical reduction of ethylene on platinum, suggesting that the dependence of the reduction rate on the degree of the surface coverage by the modifying metal varies according to the size of the modifying metal atoms.

EXPERIMENTAL

Platinum black was prepared in the conventional manner from H_2PtCl_6 solution by reduction with formaldehyde. For lowering the specific surface area, the platinum black was sintered to an extent by heating it in nitrogen stream at 350°C for an hour. The modifying metals were

deposited on the platinum black surface by stirring 1 g of the latter in 50 ml of water, adding the desired quantity of a salt of the metal in question, and acidifying the solution with HCl (in the case of bismuth, the total HCl concentration was 1 mol l^{-1} for preventing hydrolysis). The suspension, stirred vigorously by means of a magnetic stirrer, was bubbled with hydrogen for 10 min, then it was heated up to 50°C, and hydrogen was introduced for 2·5 h. The equilibrium hydrogen potential established on the catalyst surface at which ad-atoms of the metal deposited on the platinum black surface. The platinum black then was filtered out on a glass filter under protective hydrogen atmosphere, washed with distilled water, pre-dried with nitrogen stream, and dried in a drier on air at 60°C. The hydrogenations of 2-phenyl-1-propene and 1-hexene were conducted in ethanol, toluene, and in part also in benzene at 20°C and atmospheric pressure as described previously[4]. The free platinum black surface area was determined by the electrochemical potentiodynamic method also described in the paper[4].

RESULTS AND DISCUSSION

Owing to the equilibrium potential of deposition of the modifying metals ($E_{eq} <$ $< 0·00$ V) and the potential of the platinum black suspension in the medium used ($E_{eq} \approx 0·00$ V), the deposited metals were present on the platinum surface in the form of ad-atoms only. The number of surface platinum atoms covered by a deposited ad-atom of the modifying metal on disperse platinum blacks is different from that on smooth electrodes[5,6]. This is apparent from Fig. 1, where the dependences of the actual degrees of the surface coverage by the metal are plotted against the theoretical, calculated assuming that all the metal from the solution phase is completely reduced and deposited in the form of ad-atoms and that a lead and thallium ad-atom covers two platinum atoms, a bismuth ad-atom covers three platinum atoms. As is apparent, the first deposited ad-atoms of the metal (particularly lead) block a higher number of platinum atoms than they do on smooth electrodes, especially in the case of platinum black with a large surface area. At higher degrees of coverage, $\Theta_{Me} \geqq$ $\geqq 0·2 - 0·3$, the additional deposited ad-atoms cover approximately the same number of platinum atoms as on smooth surfaces. Thallium behaves in a somewhat different manner, the actual degree of coverage being for $\Theta_{Tl} > 0·5$ lower than that calculated from the atomic radii values.

Hydrogenation of 1-hexene and 2-phenyl-1-propene in all the solvents is a zero order reaction with respect to the substrate concentration, both on platinum and platinum-metal blacks. The 1-hexene hydrogenation rates in both solvents decrease with increasing amount of the deposited modifying metal. For 2-phenyl-1-propene in ethanol the dependence is similar, but in toluene and benzene the rate does not vary appreciably at low degrees of the platinum surface coverage by the modifying metal, and only starts to decrease from $\Theta_{Me} > 0·4$.

These dependences expressed in terms of the specific hydrogenation rate r_{sp} (rate per unit free surface area of unoccupied platinum) and the relative (with respect to the rate on pure platinum black) hydrogenation rate r_r are depicted in Figs 2 − 5. The dependence of the specific reaction rate on the degree of the surface coverage

by the modifying element indicates that at low Θ_{Me} values, r_{sp} even increases with increasing Θ_{Me}, particularly in the case of 2-phenyl-1-propene, and drops appreciably only at $\Theta_{Me} \geqq 0.4 - 0.6$.

Comparing the experimental dependences of the hydrogenation rates with the theoretical dependences calculated assuming that one (Figs 3 and 5, curves 1) or two (curves 2) free platinum sites must be available in the rate-determining step, we can see that a simple reaction model, based on the hypothesis that the particles that take part in the reaction are those adsorbed on neighbouring sites of unoccupied platinum (and the rate then should not exceed that corresponding to curve 2), is inconsistent with the experiment.

Taking into account the nature of the substrate to be hydrogenated, we can interpret the hydrogenation dependences in terms of the suggested mechanism[7,8] of hydrogenation of double bonds-containing substances. According to this concept, the adsorbed parts of the hydrogenated substance and the adsorbed hydrogen participate
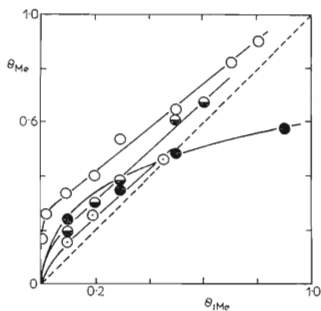

FIG. 1

Dependence of the actual degree of covering Θ_{Me} on the theoretical degree of covering of the surface by the modifying metal (Θ_{tMe}). Pt$_1$ platinum black with the specific surface area 22·9 m^2 g^{-1}, Pt$_2$ platinum black with the specific surface area 9·1 m^2 . . g^{-1}; ○ Pt$_1$–Pb, ⊙ Pt$_2$–Pb, ● Pt$_1$–Tl, ◒ Pt$_1$–Bi
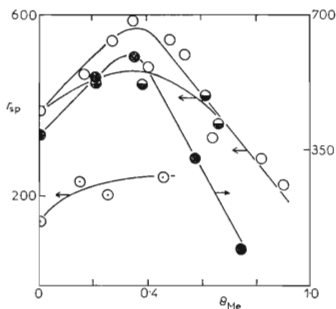
FIG. 2

Dependence of the specific hydrogenation rate r_{sp} (ml$_{H_2}$ min^{-1} g^{-1} (1 − Θ_{Me})$^{-1}$) on the degree of coverage of the surface by the modifying metal Θ_{Me}. Hydrogenation of 2-phenyl-1-propene in toluene. ○ Pt$_1$–Pb, ⊙ Pt$_2$–Pb, ● Pt$_1$–Tl, ◒ Pt$_1$–Bi

in the hydrogenation according to the scheme

$$H_2 \rightleftharpoons 2 H_{ad} \qquad (A)$$

$$R_1-CH=CH-R_2 \rightleftharpoons R_1-\underset{*}{CH}-\underset{*}{CH}-R_2 \qquad (B)$$

$$R_1-\underset{*}{CH}-\underset{*}{CH}-R_2 + H_{ad} \rightarrow R_1-\underset{*}{CH}-CH_2-R_2 \qquad (C)$$

$$R_1-\underset{*}{CH}-CH_2-R_2 + H_{ad} \rightarrow R_2-CH_2-CH_2-R_2 \qquad (D)$$
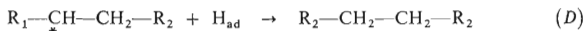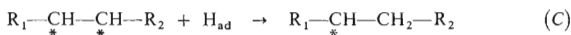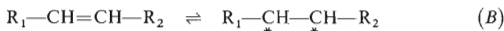
the step (C) (ref.[7]) or (D) (ref.[9]) being the slow one. The hydrogenation rate can then be written as[7]

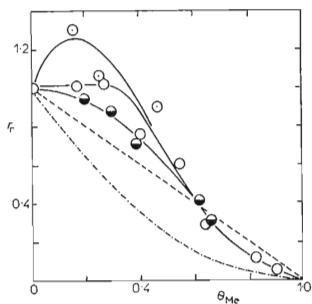$$r = k\Theta_H\Theta_R \exp\left[\beta(\Delta Q_H^0 + \Delta Q_R^0)/RT\right], \qquad (1)$$

FIG. 3

Dependence of the relative hydrogenation rate r_r on the degree of coverage by the modifying element Θ_{Me}. Hydrogenation of 2-phenyl-1-propene in toluene. ○ Pt_1–Pb, ◉ Pt_2–Pb, ● Pt_1–Bi. Theoretical curves: - - - - for $r = k(1 - \Theta_{Me})$, - · - · - for $r = k(1 - \Theta_{Me})^2$
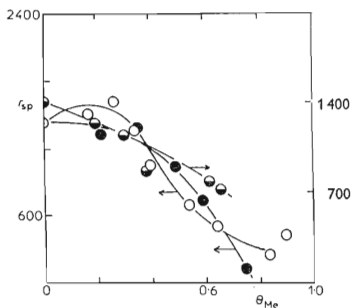
FIG. 4

Dependence of the specific hydrogenation rate r_{sp} ($ml_{H_2} \min^{-1} g^{-1}$ $(1 - \Theta_{Me})^{-1}$) on the degree of coverage of the surface by the modifying metal Θ_{Me}. Hydrogenation of 1-hexene in ethanol. ○ Pt_1–Pb, ● Pt_1–Tl, ◉ Pt_1–Bi

where Θ_H and Θ_R are the degrees of the surface coverage by hydrogen and by the organic substrate, respectively, ΔQ_H^0 and ΔQ_R^0 are terms involving the effect of the changes in the adsorption energy for a simultaneous adsorption of the two chemisorbed reactants on the activation energy of the reaction, and β is a coefficient. Eq. (1) can be rewritten as

$$r = k_N N_H N_R \exp\left[-\beta(\Delta Q_H^0 + \Delta Q_R^0)/RT\right], \qquad (2)$$

where N_H and N_R are the numbers of atoms of surface platinum occupied by the adsorbed hydrogen and by the organic substrate, respectively.

Molecules of the substances to be hydrogenated, 1-hexene and 2-phenyl-1-propene are relatively bulky, so that although being only bonded to one or two platinum atoms[1], they sterically cover a far larger number of platinum atoms (the number of the blocked adsorption sites can be estimated[9] to more than $8-12$). It is reasonable to assume that at low degrees of the surface coverage by modifying ad-atoms the number of the adsorbed substrate molecules is the same as on pure platinum surface. The adsorption of hydrogen, on the hand, decreases proportionally to the increasing coverage, because hydrogen cannot be adsorbed on sites occupied by the ad-atoms of the modifying metal. Under such assumptions the degrees of the coverage can be represented as

$$\Theta_H' = N_H/(N_{Pt}^0 - N_{Me}) \qquad (3)$$

$$\Theta_R' = N_R/N_{Pt}^0 \qquad (4)$$
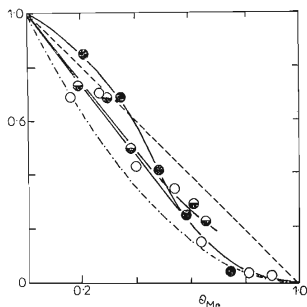
$$\Theta_{Me}' = N_{Me}/N_{Pt}^0 . \qquad (5)$$

FIG. 5

Dependence of the relative hydrogenation rate r_r on the degree of coverage of the surface by the modifying metal Θ_{Me}. Hydrogenation of 1-hexene in ethanol. $\circ$ Pt_1–Tl, $\bullet$ Pt_1–Bi. Theoretical curves: $---- \, r = k(1 - \Theta_{Me})$, $-\cdot-\cdot-\cdot- \, r = k(1 - \Theta_{Me})^2$

Inserting these relations into Eq. (2) we obtain relations for the hydrogenation rate on the modified surface,

$$r' = k_N N_{Pt}^{02} (1 - N_{Me}/N_{Pt}^0) \, \Theta_H' \Theta_R' \exp\left[-\beta(\Delta Q_H' + \Delta Q_R')/RT\right], \qquad (6)$$

and for the specific hydrogenation rate,

$$r_{sp}' = r'/N_{Pt}^{02}(1 - \Theta_{Me}') = k_N \Theta_H' \Theta_R' \exp\left[-\beta(\Delta Q_H' + \Delta Q_R')/RT\right]. \qquad (7)$$

For the specific rate on nonmodified platinum we can write similarly

$$r_{sp} = r/N_{Pt}^{02} = k_N \Theta_H^0 \Theta_R^0 \exp\left[-\beta(\Delta Q_H^0 + \Delta Q_R^0)/RT\right], \qquad (8)$$

and the ratio of the specific rates is

$$r_{sp}'/r_{sp} = r'(1 - \Theta_{Me}')^{-1}/r =$$
$$= \Theta_R' \Theta_H'/\Theta_R^0 \Theta_H^0 \exp\left\{-\beta[(\Delta Q_H' - \Delta Q_H^0) + (\Delta Q_R' - \Delta Q_R^0)]/RT\right\}. \qquad (9)$$

Under the above assumption, we also have $\Theta_H' \Theta_R' = \Theta_H^0 \Theta_R^0$. The experimental heats of hydrogen adsorption on platinum black modified by copper[10] indicate that $\Delta Q_H' < \Delta Q_H^0$, and it is reasonable to assume that similarly, $\Delta Q_R' < \Delta Q_R^0$. This implies that the exponential term in Eq. (9) exceeds unity and so the specific hydrogenation rate in dependence on the degree of the platinum surface coverage by the modifying ad-atoms can even increase at lower Θ_{Me} values (in the region of validity of Eq. (4)). The actual shape of the dependences will depend on the Θ_{Me} region over which the relation (4) holds true and on the extent to which the modification of the surface will affect the adsorption energies of the two reactants. Generally it can be assumed that the beginning of the decrease in r_{sp} should shift to higher Θ_{Me} values as bulkier substrate molecules are hydrogenated. The solvent type may also be of significance, as it affects the change in the adsorption heats of the two reactants and also can affect the orientation of the adsorbed substrate and thereby the number of sites on the platinum surface occupied by the substrate molecules.

Comparing the results with the previous studies of hydrogenation of 2-phenyl-1-propene (ref.[4]) and of 1-hexene and other olefinic hydrocarbons[10] on platinum black modified by copper, we find them in a way different. On copper-modified platinum black the r_{sp} values have been observed not to increase with increasing Θ_{Me}, but to drop rapidly at $\Theta_{Me} \geqq 0.2 - 0.3$. This different behaviour may be due to the copper occurring on the platinum surface predominantly as the bulk metal phase rather than as ad-atoms, so that the substrate probably cannot adsorb on the sites occupied by this copper metal.

REFERENCES

1. Sokolskii D. V., Sokolskaya A. M.: *Metally — Katalizatory Gidrogenizatsii*. Izd. Nauka Kaz. SSR, Alma Ata 1970.
2. Mallat T., Petró J., Schaffer M.: Acta Chim. (Budapest) *98*, 175 (1978).
3. Červený L., Paseka I., Stuchlý V., Růžička V.: This Journal, in press.
4. Paseka I., Červený L., Mach J., Růžička V.: This Journal *45*, 3541 (1980).
5. Furuya N., Motoo S.: J. Electroanal. Chem. Interfacial Electrochem. *98*, 189 (1979).
6. Furuya N., Motto S.: J. Electroanal. Chem. Interfacial Electrochem. *100*, 771 (1979).
7. Vassiliev Yu. B., Bagotzky V. S., Khazova O. A., Cherny V. V., Meretsky A. M.: J. Electro-anal. Chem. Interfacial Electrochem. *98*, 273 (1979).
8. Fujikawa K., Kita H., Miyahara K., Sato S.: J. Chem. Soc., Faraday Trans. 1, *71*, 1573 (1975).
9. Gileadi E.: Modern Aspects of Electrochemistry, *1966*, 4.
10. Stuchlý V.: *Thesis*. Prague Institute of Chemical Technology, Prague 1980.

Translated by P. Adámek.