HYDROGENATION OF CYCLOPENTADIENE IN BINARY MIXTURES WITH UNSATURATED HYDROCARBONS OVER PALLADIUM AND PLATINUM BLACKS

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It was shown previously that, over Raney nickel, cyclopentadiene is selectively hydrogenated in its binary mixtures with cyclopentene, cyclohexene, 1-octene, and diphenylacetylene. The second components begin to combine with hydrogen only after conversion of cyclopentadiene to cyclopentene is complete. In its binary mixtures with styrene, piperylene, and 1-heptene, cyclopentadiene is hydrogenated nonselectively [1]. In the present investigation we have studied the hydrogenation of cyclopentadiene in binary mixtures with unsaturated hydrocarbons over palladium and platinum blacks.

EXPERIMENTAL

Reaction was carried out with 0.002 mole* of substance in the liquid phase at 25° at atmospheric pressure in presence of 0.1 g of palladium black or 0.045 g of platinum black. In the experiments with palladium cyclohexane was used as solvent, and in the experiments with platinum 96% ethanol was used. The experimental conditions were such that reaction occurred in the kinetic region; further details of the experimental conditions are given in the table. A detailed description of the procedure is given in a previous communication [1]. The blacks were prepared by reduction of palladium and platinum chlorides in aqueous solution by formaldehyde in presence of alkali. The completeness of the hydrogenation of cyclopentadiene into cyclopentene was checked in parallel experiments by the qualitative reaction with hydroquinone [2]. The extent of hydrogenation was calculated from the volume of hydrogen actually consumed and the volume theoretically required for conversion into cyclopentene.

Hydrogenation of the Individual Components of the Mixture over Palladium Black

For comparison purposes, we first studied the rate of hydrogenation of each unsaturated compound separately under the same experimental conditions. The results are given in the table and are represented by kinetic curves (Fig. 1) on which the total volume of hydrogen consumed \( \left( \frac{\Sigma V}{2} \right) \) is plotted as abscissa and the rate of absorption of hydrogen in milliliters per half-minute \( \left( \frac{\Delta V}{\Delta t} \right) \) as ordinate. It will be seen from these curves that the hydrogenation of cyclopentadiene, cyclopentene, styrene, cyclohexene, and diphenylacetylene proceed in accordance with a zero-order law (Curves 1-5). The rate of reaction remains constant until 40-70% of the theoretically necessary volume of hydrogen has been absorbed. With respect to rate of addition of hydrogen, the hydrocarbons form the series cyclopentadiene > styrene > cyclopentene > diphenylacetylene > cyclohexene, the relative values of the constants being 11.4 : 5.6 : 5.2 : 4.7 : 3.8 (Experiments 1-5).

Hydrogenation of Binary Mixtures in Presence of Palladium Black

The mixtures taken for hydrogenation contained cyclopentadiene and the other unsaturated component in a molar ratio of 1 : 2. The kinetic curves for the hydrogenation of binary mixtures are given in Fig. 2, from

* In Experiments 13 and 14 0.004 mole was used.
which it can be seen that the mixtures are again hydrogenated in accordance with a zero-order law. In all cases
the rate of hydrogenation of the mixture is considerably lower than the sum of the rates of hydrogenation of the
components taken separately. We showed previously that over palladium black—as also over Raney nickel—one of the two conjugated double bonds of cyclopentadiene is hydrogenated selectively [3]. It could be expected
that, also in binary mixtures with compounds containing an isolated double bond, cyclopentadiene would be hy-
drogenated selectively to cyclopentene.

![Graph 1](image1)

**Fig. 1.** Hydrogenation of cyclopentadiene (1), cyclopentene (2), styrene (3), diphenylacetylene (4), and cyclohexene (5) in cyclohexane over palladium black.

![Graph 2](image2)

**Fig. 2.** Hydrogenation of binary mixtures of cyclopentadiene with styrene (1), cyclohexene (2), and diphenylacetylene (3) in cyclohexane over palladium black.

It can be seen from Fig. 2 that the kinetic curve for the hydrogenation of a mixture of cyclopentadiene
and cyclohexene (Curve 2) has a characteristic inflection corresponding to the point at which one molecular
proportion of hydrogen (26.4 ml; the theoretical amount is 24.1 ml) has added, but the kinetic curves for
mixtures of cyclopentadiene with diphenylacetylene (Curve 3, Experiment 8) and with styrene (Curve 1, Experi-
ment 10) have inflections corresponding to two and more than two molecular proportions hydrogen. It may be
supposed that in admixture with cyclohexene, cyclopentadiene is hydrogenated selectively, whereas in mixtures
with styrene and diphenylacetylene simultaneous hydrogenation occurs. In order to confirm this supposition we
carried out parallel experiments in which the solution was tested for cyclopentadiene with hydroquinone when
the volume of hydrogen necessary for the conversion of cyclopentadiene into cyclopentene had been consumed.
It was found that, in the binary mixture with cyclohexene (Experiment 7), no cyclopentadiene could be detected
in the solution when 102% of the theoretical amount of hydrogen had been consumed. In the binary mixture
with diphenylacetylene there was still a positive test for cyclopentadiene when 175.2% of the theoretical amount
of hydrogen had been consumed (Experiment 9). Only after the absorption of double the volume of hydrogen
necessary for the hydrogenation of cyclopentadiene into cyclopentene was cyclopentadiene found to be absent
from the solution. In the mixture with styrene the test for cyclopentadiene was still positive after the addition
of 55 ml of hydrogen, i.e., 216% of the amount necessary for hydrogenation into cyclopentene (Experiment 11).

Hence, in presence of palladium black, as also of Raney nickel, cyclopentadiene in binary mixtures with