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Abstract

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Catalysis of Hydrogenation Reactions by Zinc

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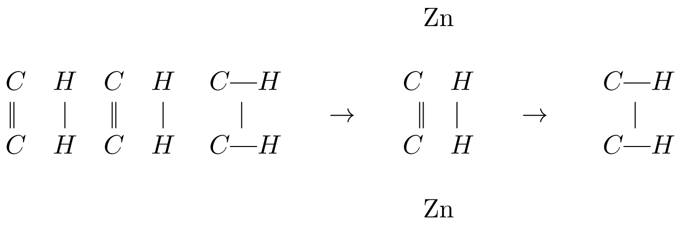
At present, the view is widely accepted according to which a heterogeneous catalytic reaction proceeds through an adsorption stage. If, in the course of hydrogenation, both components of the reaction are activated, then they form a surface intermediate complex with the catalyst. In this case the ease of hydrogenation of various interatomic bonds depends on the height of the energy barrier ($-E$) of the reaction (^{1}). The reaction that should occur first is the one with the lowest height of the energy barrier for formation (or decomposition) of the intermediate complex. The values of E can be calculated from the mean values of bond energies (Q). Thus, for example, for hydrogenation reactions of $C=C$, $C\equiv C$, and $C=O$ bonds on a Ni catalyst, they are respectively: $-E_{C=C} = 2.9$ kcal, $-E_{C\equiv C} = -7.4$ kcal, and $-E_{C=O} = 13.1$ kcal. In accordance with this, $C\equiv C$ and $C=C$ bonds on Ni are indeed hydrogenated more readily than $C=O$. In an analogous sequence these reactions proceed on almost all known catalysts.

An entirely different picture is observed on Zn, on which the $C=C$ bond, as a rule, is not hydrogenated, the $C=O$ group is hydrogenated to CH—OH, and the acetylene bond selectively to the ethylene bond.

Let us consider whether the interesting features of Zn can also be explained by the relative height of the energy barriers of reactions on this catalyst. Hydrogenation of an ethylene bond on Zn with formation of an intermediate complex is represented by the scheme:



$$\begin{array}{ccccccccc} & & & & & \text{Zn} & & & \\ C & H & C & H & C{-}H & & C \quad H & & C{-}H \\ \| & | & \| & | & | & \rightarrow & \| \quad | & \rightarrow & | \\ C & H & C & H & C{-}H & & C \quad H & & C{-}H \\ & & & & & \text{Zn} & & & \end{array}$$

The heat of its formation:

$$E_1' = -Q_{C=C} - Q_{H-H} + 2Q_{\equiv C-Zn} + 2Q_{H-Zn} =$$

$$= -46.7 - 104.2 + 2 \cdot 27 + 2 \cdot 19.5 = -57.9 \text{ kcal/mol.} \tag{I}$$

The heat of its decomposition:

$$E_1'' = -2Q_{\equiv C-Zn} - 2Q_{H-Zn} + 2Q_{C-H} =$$

$$= -2 \cdot 27 - 2 \cdot 19.5 + 2 \cdot 90.5 = 88 \text{ kcal/mol.}$$

Similarly, for the reaction of hydrogenation of an acetylene bond to an ethylene bond, the heat of formation is

$$E_2' = -Q_{C\equiv C} - Q_{H-H} + 2Q_{\equiv C-Zn} + 2Q_{H-Zn} =$$

$$= -37.4 - 104.2 + 2 \cdot 27 + 2 \cdot 19.5 = -48.6 \text{ kcal/mol.} \tag{II}$$

The heat of decomposition:

$$E_2'' = -2Q_{\equiv C-Zn} - 2Q_{H-Zn} + 2Q_{=C-H} = -54 - 39 + 181 = 88 \text{ kcal/mol.}$$

Doublet scheme of the reduction reaction of the C=O group:

(schematic reaction diagram)

Heat of formation of the complex:

$$\begin{aligned} E_3' &= -Q_{C=O} - Q_{H-H} + Q_{=C-Zn} + Q_{O-Zn} + 2Q_{H-Zn} = \\ &= -83.4 - 104.2 + 27 + 74.2 + 2 \cdot 19.5 = -47.4 \text{ kcal/mole.} \end{aligned} \tag{III}$$

Heat of its decomposition:

$$E_3'' = -Q_{C-Zn} - Q_{O-Zn} - 2Q_{H-Zn} + Q_{C-H} + Q_{O-H}$$

$$= -27 - 74.2 - 2 \cdot 19.5 + 90.5 + 110.4 = 60.7 \text{ kcal/mole.}$$

Instead of $Q_{=C-Zn}$ and $Q_{\equiv C-Zn}$, for which there are no data in the literature, the somewhat smaller bond energy Q_{-C-Zn} was taken, which probably does not affect the main conclusion.

As we see, for all three reactions $E' < 0$, while $E'' > 0$. Consequently, the rate of these processes should be limited by the adsorption stage (1). From the approximate calculations given above it follows that the energy barriers of the reactions considered on Zn are considerably higher than on Ni. If one assumes that $E = -\frac{4}{3}\varepsilon$, then their activation energies are, respectively, 43, 39, and 26 kcal/mole. Changing the sign in E from + to −, we obtain: $-E_{C=C} = 57.9$ kcal/mole; $-E_{C\equiv C} = 48.6$ kcal/mole; $-E_{C=O} = 47.4$ kcal/mole. These results make it possible to predict that on Zn all three reactions should proceed with greater difficulty than on Ni and other metallic catalysts of hydrogenation processes. Since $|E'_1| > |E'_2| > |E'_3|$, the ethylene bond should be hydrogenated with the greatest difficulty, and the C=O bond more readily. The values of the bond energies were taken as follows: for Q_{H-Zn} from (^{2}), the rest from (^{3}). Q_{O-Zn} was calculated in our laboratory.

Analysis of equations (I)—(III) shows that the larger values of E' on Zn in comparison with E' on Ni are due to the fact that Q_{H-Zn} (19.5 kcal) $\ll Q_{H-Ni}$ (55 kcal), although Q_{-C-Zn} (27 kcal) $> Q_{=C-Ni}$ (19 kcal), and Q_{O-Zn} (74.2 kcal) $> Q_{O-Ni}$ (48.3 kcal). This permits the assumption that the ratio of the concentrations of active hydrogen and of the hydrogenated compound on Zn is lower than on Ni.

Experimental Part

The catalyst was prepared by leaching turnings or thin plates of a Zn—Al alloy (weight ratio 1:1) with a 3% aqueous solution of sodium hydroxide until the evolution of hydrogen ceased; it was then washed with water to a neutral reaction toward phenolphthalein and loaded moist into the reactor. The catalyst was found to contain 5% residual Al. In all operations we endeavored to avoid contact of the catalyst with air. Experiments at normal pressure were carried out under flow conditions. The compound to be hydrogenated (and hydrogen in large excess) was passed over the catalyst at a space velocity of 0.1—0.2. In experiments under pressure the reaction was carried out in a rotating autoclave. The catalyst was usually used once. The unsaturation of the catalysts and the content of carbonyl groups in them were determined by the oxime method. Unsaturation was characterized by the volume of hydrogen consumed for hydrogenation of a weighed portion of catalyst on skeletal nickel at 20°. In other cases the catalysts were also analyzed by gas-liquid chromatography or by fractionation on a column. The constants of the isolated reaction products were determined.

Table 1 shows the conditions under which three types of bonds (C=C, C C, C=O) in the compounds we studied begin to be hydrogenated.

Hydrogenation of the ethylenic bond. At temperatures up to 200°, 2- and 3-octenes were recovered unchanged. 1-Octene and cyclohexene were not hydrogenated even under a pressure of 100 atm at 150°.

Table 1

Hydrogenated compound	Main reaction product	Hydrogenated bond	Temp., °C*	Pressure, atm.*
$CH_3CH_2CH_2CH_2CH_2CH_2CH=CH_2$	Not hydrogenated	α-C=C	150	100
$CH_3CH_2CH_2CH_2CH_2CH=CHCH_3$	Not hydrogenated	β-C=C	200	Norm.
$CH_3CH_2CH_2CH_2CH=CHCH_2CH_3$	Not hydrogenated	γ-C=C	200	Norm.
cyclohexene	Not hydrogenated	Cycl. C=C	150	100
$C_6H_5CH=CH_2$	$C_6H_5C_2H_5$	Active C=C	100	Norm.
methylcyclopropyl ketone, $CH_3-C(=O)-CH-CH_2-CH_2$	$CH_3CHOHCH-CH_2-CH_2$	C=O	90	130
$CH\ CH$	$CH_2=CH_2$	C C	65	Norm.
$C_6H_5C\ CC_6H_5$	$C_6H_5CH=CHC_6H_5$	C C	60	Norm.
$CH_2=CHC\ CH$	$CH_2=CH-CH=CH_2$	C C	60	Norm.
$CH_2=C-C\ CH\ CH_3$	$CH_2=C-CH=CH_2\ CH_3$	C C	50	Norm.
$CH\ C-C(OH)(CH_3)-CH_3$	$CH_2=CH-CH(CH_3)-CH_3\ OH$	C C	50	Norm.
$CH_2=CHC\ C-C(OH)(CH_3)-CH_3$	$CH_2=CH-CH_2-CH_2-C(OH)(CH_3)-CH_3$	C C	80	100
$HOCH_2-C\ C-CH_2OH$	$CH_2OH-CH=CH-CH_2OH$	C C	130	90
$CH_2=C-CH=CH_2\ OH$	Not hydrogenated	Active C=C	140	Norm.
$CH_3CH=CHCH=CH_2$	CH_3- $CH_2=CH_2$ $-CH-CH_2$	Active C=C	100	50

Hydrogenated compound	Main reaction product	Hydrogenated bond	Temp., °C*	Pressure, atm.*
bicyclic ketone, CH_3C–C=O with HC/CH_2 ring and $CHCH_3$	CH_3–C–CHOH with HC/CH_2 ring and CH–CH_3	C=O	50	Norm.
$C_6H_5CH=CH$ –C(=O)–H	$C_6H_5CH=CHCH_2OH$	**C=O**	60	Norm.
$CH_3C=CHCH_2CH_2C(=O)CH_3$	CH_3CH $CH_2CH_2CH_2C(=O)CH_3$ CH_3	C=C	100	Norm.

* Process conditions under which the given compound begins to be hydrogenated on a zinc catalyst.

At temperatures below 100° and normal pressure, styrene does not add hydrogen. Above 170° the reaction rate increases sharply. At 250° the degree of hydrogenation of styrene reaches 98%. The catalyst was distilled off in vacuum and consisted of almost pure ethylbenzene: b.p. 135°/740 mm, n_D^{20} 1.4950; d_4^{20} 0.8660. The residue after distillation was insignificant. In an experiment under a pressure of 100 atm at 100°, styrene completely polymerized in 3 hours. Zinc also does not catalyze the hydrogenolysis of the trimethylene ring of methylcyclopropyl ketone (4), which on other metals readily interacts with hydrogen, imitating the behavior of a double bond (5).

Hydrogenation of diene hydrocarbons. Piperylene and isoprene at normal pressure and temperatures up to 140° were not hydrogenated on Zn (6). Piperylene was not hydrogenated even at a hydrogen pressure of 50 atm at 100°. At 80 atm the unsaturation of the catalyst de-

decreased by 15%; at 100 atm, by 28%; and at 100 atm and 150° it decreased by a factor of two, which corresponds to complete hydrogenation of one double bond.

Thus, hydrogenation on Zn makes it possible to recognize the double bond of styrene and a conjugated double bond, as distinct from an unactivated ethylenic bond.

Hydrogenation of the acetylenic bond. The triple bond in acetylene, vinylacetylene, isopropenylacetylene, dimethylethynylcarbinol, and tolane (6) was selectively hydrogenated on Zn to a double bond at normal pressure. Below 50–65° the reaction does not proceed. Hydrogenation of the acetylenic bond of dimethylvinylethynylcarbinol and but-2-yne-1,4-diol was accomplished under pressure (90–100 atm) at 80–130°. Thus, Zn catalyzes the hydrogenation of the acetylenic bond in compounds of various structures. The reaction proceeds under more severe conditions than on Ni.

Reduction of the carbonyl group. Aldehydes and ketones (^{7}) begin to be reduced on Zn at 50–60° and normal pressure, i.e., under approximately the same conditions as on skeletal nickel. α,β-Unsaturated aldehydes and ketones are selectively reduced to the corresponding unsaturated alcohols (^{8}). Methylcyclopropyl ketone is likewise reduced only at the C=O group (^{4}). It should be noted that zinc does not always exhibit selectivity of action. Thus, in the reduction of 2-methylhept-2-en-6-one, in which the C=C bond is remote from the C=O group, Zn did not show selectivity: chiefly the C=C bond was hydrogenated. Above 60–80° the selectivity of the reduction of α,β-unsaturated aldehydes and ketones begins to be impaired: the content of double bond in the catalyst rapidly decreases (^{8}). It may be supposed that these anomalies are associated with features of the structure of the compounds being reduced (for example, absence of conjugation of bonds in the molecule), with adsorption displacement of some groups of atoms by others, or with a change in the mechanism of catalysis under the altered conditions.

A generalization of the results obtained shows the distinctive character of the catalytic action of Zn in hydrogenation and reduction reactions. Zinc does not catalyze the hydrogenation of olefins, and hydrogenation of an ethylenic bond activated by a phenyl group or by a conjugated double bond is accelerated only at elevated temperatures or under pressure. Zn catalyzes selective hydrogenation of an acetylenic bond to an ethylenic bond and especially accelerates reduction of the C=O group of aldehydes and ketones. The results obtained agree with the calculated values of the energy barriers of these reactions on zinc. Thus, the different sequence of hydrogenation of bonds observed on Zn, as compared with other metallic catalysts, can also be explained by the mechanism of formation of an intermediate complex.

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Note: Figure translations are in progress. See original paper for figures.