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# A Mechanistic Study of Cyclohexene Hydrogenation over Platinum Catalyst Using the Predicate Calculus of Mathematical Logic

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By combining the available experimental information with the assumed mechanism of complex processes, mathematical logic allows proper selection of the necessary and sufficient steps to be included in the adequate mechanism, i.e., correct interpretation of the experimental information. This procedure requires that the expected outcomes of the experiments be formulated as two, mutually exclusive, possibilities. Furthermore, the method automatically answers the questions: (a) whether or not the assumed mechanism contains a logical inconsistency (whether or not the system of logical equations is consistent), and (b) whether or not the planned experiments are expected to provide new information concerning the adequate mechanism (whether or not the logical equation of the planned experiment yields an independent new equation in the case of the two expected outcomes).

## INTRODUCTION

The study of complex chemical reactions, e.g., catalytic hydrogenation of cyclohexene, consists of several phases in a logically determined sequence. Prior to the elucidation of the kinetic law, it is necessary to establish the so-called *adequate mechanism.*

In connection with mechanistic studies, it is useful to define the conceptions *assumed* and *adequate mechanisms.* The assumed mechanism includes all steps that occur or are likely to occur in similar reactions according to available chemical or physical evidence. The adequate mechanism is a considerably narrower notion since it only includes steps that are *necessary and sufficient* for the interpretation of the available experimental information. Thus, only the adequate mechanism can be regarded as verified. By definition, with the increase of the amount of experimental information, new steps may be added to the adequate mechanism, i.e., it may undergo modification or even profound changes.

In order to establish the adequate mechanism, it is necessary to select the steps of the assumed mechanism that can be proved to occur or not to occur during the reaction under consideration. Since this condition involves two mutually exclusive alternatives (occurs–does not occur) for each step, verification of the adequate mechanism can be performed by applying the predicate calculus of mathematical logic to the treatment of the results of properly planned experiments.

## 1. ASSUMED MECHANISM OF CYCLOHEXENE HYDROGENATION (deuteration) OVER A PLATINUM CATALYST

The mechanism of hydrogenation of unsaturated hydrocarbons over metal catalysts has been studied by several authors (1–10). On the basis of these studies, the assumed mechanism of cyclohexene hydrogenation on a platinum catalyst can be described as shown in Fig. 1.

The steps involved in the scheme are as follows:

$\overrightarrow{1}, \overrightarrow{1'}, \overrightarrow{1''}$ and $\overleftarrow{1}, \overleftarrow{1'}, \overleftarrow{1''}$ stand for the adsorption of hydrogen (deuterium), cyclohexene and cyclohexane, and for their desorptions, respectively;

2, 2′ and 2″ denote H–D exchange reactions between adsorbed hydrogen (deuterium) and cyclohexene, adsorbed cyclohexene

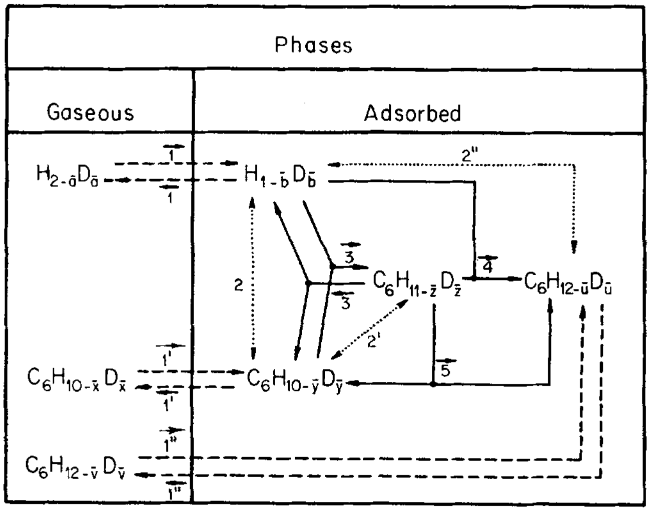


FIG. 1. The assumed mechanism of the catalytic hydrogenation (deuteration) of cyclohexene in the presence of platinum, where $0 \leq \bar{a} \leq 2$; $0 \leq \bar{b} \leq 1$, $0 \leq \bar{x} \leq 10$, $0 \leq \bar{y} \leq 10$, $0 \leq \bar{z} \leq 11$, $0 \leq \bar{u} \leq 12$, and $0 \leq \bar{v} \leq 12$ are the average numbers of deuterium atoms in 1 mole of the gaseous hydrogen–deuterium mixture, adsorbed hydrogen–deuterium atoms, gaseous cyclohexene, adsorbed cyclohexene, semihydrogenated intermediate, adsorbed cyclohexane, and gaseous cyclohexane, respectively. The 1, 1′ and 1″ denote adsorption and desorption steps, respectively; 2, 2′ and 2″ are isotope exchange, while 3, 4, and 5 are surface reactions visualized also by the different lines.

and the semihydrogenated intermediate, adsorbed hydrogen (deuterium) and cyclohexane, respectively;

$\overrightarrow{3}$ and $\overleftarrow{3}$ stand for chemical reactions between adsorbed hydrogen (deuterium) and cyclohexene yielding the semihydrogenated product;

$\overrightarrow{4}$ denotes the chemical reaction between adsorbed hydrogen (deuterium) and the semihydrogenated product;

$\overrightarrow{5}$ stands for the disproportionation of the semihydrogenated product yielding cyclohexene and cyclohexane.

(Since under the experimental conditions ($t = 30°C$) hydrogenation is practically irreversible, the reverse of both $\overrightarrow{4}$ and $\overrightarrow{5}$ have been omitted.)

## 2. EXPERIMENTAL INFORMATION

A detailed description of the experimental method was given in earlier papers (*11*). Only those experimental results are presented here which are used in the verification of the adequate mechanism. As mentioned in the "Introduction," the possible outcome of each experiment is formulated in a manner that only two, mutually exclusive, alternatives should occur. The symbols for these alternatives are ↑ and ↓. The pertinent experimental information is collected in Table 1.

## 3. FUNDAMENTAL RELATIONS OF PREDICATE CALCULUS

The following is a short summary of the principles of mathematical logic required in the subsequent discussion.

Let $B_1, B_2, \ldots B_i \ldots$ stand for predicates, each able to assume two mutually exclusive values, viz. *true* (affirmative) and *false* (negative). These two values are denoted by ↑ and ↓, respectively. We define two kinds of operations among these predicates, the results of which are also predicates. One will be called the *and* operation (conjunction), the other the *or* operation (disjunction). The operations are denoted by $\wedge$ and $\vee$, respectively. The set of predicates obtained by performing these two operations is shown in Table 2.

The following three laws are valid for $\wedge$ and $\vee$ operations, as concluded from Table 2.

TABLE 1
EXPERIMENTAL INFORMATION ON CATALYTIC HYDROGENATION (deuteration) OF CYCLOHEXENE ON PLATINUM[a]

| Symbol | Experimental information | Alternatives of the experimental result | | Experimental result |
|---|---|---|---|---|
| | | $\uparrow$ | $\downarrow$ | |
| $I_1$ | Hydrogenation (deuteration) | Occurs | Does not occur | $\uparrow$ |
| $I_2$ | H–D exchange between $C_6H_{12}$ and $D_2$ in separate experiments | Occurs | Does not occur | $\downarrow$ |
| $I_3$ | H–D exchange between gaseous $H_2$ and $D_2$ during hydrogenation | Occurs | Does not occur | $\uparrow$ |
| $I_4$ | In the initial mixture $\bar{a} = 2$ and $\bar{x} = 0$. During deuteration: | $\bar{a} < 2$ | $\bar{a} \approx 2$ | $\downarrow$ |
| $I_5$ | In the initial mixture $\bar{a} = 2$ and $\bar{x} = 0$. During deuteration: | $\bar{x} > 0$ | $\bar{x} \approx 0$ | $\uparrow$ |
| $I_6$ | In the initial mixture $\bar{a} = 2$; $\bar{x} = 0$, and $C_{v=0} = 0$. During deuteration: | $C_{v=0} > 0$ | $C_{v=0} \approx 0$ | $\uparrow$ |
| $I_7$ | In the initial mixture $\bar{a} = 2$; $\bar{x} = 0$, and $C_{v=3,4,\ldots} = 0$. During deuteration, practically regardless of the conversion: | $C_{v=3,4,\ldots} \neq 0$ | $C_{v=3,4,\ldots} \approx 0$ | $\uparrow$ |
| $I_8$ | In the initial mixture $\bar{a} = 2$, $\bar{x} = 0$, and $C_{v=2} = 0$. As a result of varying the $D_2$-pressure during hydrogenation: | $C_{v=2} = fp_{D_2}$ | $C_{v=2} \neq fp_{D_2}$ | $\uparrow$ |

[a] $C_{v=i}$ = the relative concentration of the cyclohexene fraction containing $v = i$ deuterium atoms, as determined by mass spectrometry, $p_{D_2}$ = deuterium pressure, $f$ = proportionality factor.

Commutative law:

$B_1 \wedge B_2 = B_2 \wedge B_1$ and $B_1 \vee B_2 = B_2 \vee B_1$.

Associative law:

$(B_1 \wedge B_2) \wedge B_3 = B_1 \wedge (B_2 \wedge B_3)$

and $(B_1 \vee B_2) \vee B_3 = B_1 \vee (B_2 \vee B_3)$.

Distributive law:

$B_1 \wedge (B_2 \vee B_3) = (B_1 \wedge B_2) \vee (B_1 \wedge B_3)$

and

$B_1 \vee (B_2 \wedge B_3) = (B_1 \vee B_2) \wedge (B_1 \vee B_3)$.

TABLE 2
RESULTS OF PERFORMING THE $\wedge$ AND $\vee$ OPERATION

| $B_1$ \ $B_2$ | $\uparrow$ | $\downarrow$ |
|---|---|---|
| $\uparrow$ | $\uparrow$ | $\downarrow$ |
| $\downarrow$ | $\downarrow$ | $\downarrow$ |
| | $B_1 \wedge B_2$ | |

| $B_1$ \ $B_2$ | $\uparrow$ | $\downarrow$ |
|---|---|---|
| $\uparrow$ | $\uparrow$ | $\uparrow$ |
| $\downarrow$ | $\uparrow$ | $\downarrow$ |
| | $B_1 \vee B_2$ | |

### 4. Determination of the Adequate Mechanism

In order to interpret the individual pieces of information, it is necessary to include or exclude various steps of the assumed mechanism (Fig. 1). From the viewpoint of logic, a step may be *absolutely* or *alternatively necessary*.

The applicability of mathematical logic is obvious on the basis of the above considerations. The individual steps and the experimental information can be regarded as predicates with two alternatives. One of the alternatives corresponds to the true (↑) predicate, i.e., the given step occurs, takes place, is involved, etc. The other alternative corresponds to the false (↓) predicate, i.e., the step under consideration does not occur, does not take place, is not involved, etc. The two kinds of logical connection between steps can be identified with the $\wedge$ (absolutely necessary) and the $\vee$ (alternatively necessary) operation, respectively.

Thus, in order to interpret experimental information $I_1$–$I_8$, the following "system of equations" can be written on the basis of Fig. 1 and Table 1:

$$I_1 = \overrightarrow{1} \wedge \overrightarrow{1'} \wedge \overleftarrow{1''} \wedge \overrightarrow{3} \wedge (\overrightarrow{4} \vee \overrightarrow{5}), \quad (1)$$

$$I_2 = \overrightarrow{1} \wedge \overleftarrow{1} \wedge \overrightarrow{1''} \wedge \overleftarrow{1''} \wedge 2'', \quad (2)$$

$$I_3 = I_1 \wedge \overleftarrow{1}, \quad (3)$$

$$I_4 = I_1 \wedge \{I_2 \vee [\overleftarrow{1} \wedge (2 \vee \overleftarrow{3})]\}, \quad (4)$$

$$I_5 = \overrightarrow{1} \wedge \overrightarrow{1'} \wedge \overleftarrow{1'} \wedge \overrightarrow{3} \wedge \overleftarrow{1''} \wedge \{\overrightarrow{5} \vee [\overrightarrow{4} \wedge (2 \vee 2' \vee \overleftarrow{3})]\}, \quad (5)$$

$$I_6 = \overrightarrow{1} \wedge \overrightarrow{1'} \wedge \overleftarrow{1''} \wedge 2' \wedge \overrightarrow{3} \wedge \overrightarrow{5}, \quad (6)$$

$$I_7 = I_1 \wedge (2 \vee 2' \vee 2'' \vee \overleftarrow{3}), \quad (7)$$

$$I_8 = \overrightarrow{1} \wedge \overrightarrow{1'} \wedge \overleftarrow{1''} \wedge \overrightarrow{3} \wedge \overrightarrow{4}. \quad (8)$$

The correctness of the above "system of equations" in the case of ascribing the ↑ value to each information can be verified by the following considerations based on Fig. 1.

The occurrence of hydrogenation ($\uparrow I_1$) is absolutely necessary, therefore, it requires that the adsorption of hydrogen and cyclohexene ($\overrightarrow{1}$ and $\overrightarrow{1'}$), the desorption of the product cyclohexane ($\overleftarrow{1''}$), and the first step of the surface reaction ($\overrightarrow{3}$) be connected by the $\wedge$ operation. The reaction can be completed via either step $\overrightarrow{4}$ or $\overrightarrow{5}$. Therefore these are connected by the $\vee$ operation and the resulting element is connected to the preceding steps by the $\wedge$ operation.

The H–D exchange between $D_2$ and cyclohexane in a separate experiment can only occur ($\uparrow I_2$) if, as absolutely necessary steps, one connects the adsorption and desorption of hydrogen (deuterium) ($\overrightarrow{1}$ and $\overleftarrow{1}$) and of cyclohexane ($\overrightarrow{1''}$ and $\overleftarrow{1''}$), and the H–D exchange reaction ($2''$) by the $\wedge$ operation.

In order to account for the H–D exchange between gaseous $H_2$ and $D_2$ ($\uparrow I_3$), it is necessary to connect information $\uparrow I_1$ and the hydrogen (deuterium) desorption step ($\overleftarrow{1}$) by the $\wedge$ operation.

Information $\uparrow I_4$ means that if deuteration is started with pure $D_2$, HD and $H_2$ molecules will appear in the gas phase during the reaction. Thus, it is required that informations $\uparrow I_1$ and $\uparrow I_2$ be connected by the $\wedge$ operation since this provides a route for hydrogen to the gas phase. Another alternative is that adsorbed hydrogen (deuterium) participates in one of the H–D exchange steps, or reactions leading to H–D exchange (2 and $\overleftarrow{3}$) and, at the same time, hydrogen desorption ($\overleftarrow{1}$) also occurs. Therefore, $I_2$ should be connected with step $\overleftarrow{1}$ by the $\vee$ operation while the latter is connected with either 2 or $\overleftarrow{3}$ ($\vee$ operation) by the $\wedge$ operation.

If the cyclohexene originally containing only hydrogen becomes enriched in deuterium during hydrogenation ($\uparrow I_5$), the number of steps required by information $\uparrow I_1$ should be extended in such a manner that step $\overrightarrow{4}$ be connected by an $\wedge$ operation with one of the steps yielding deuterium-containing adsorbed cyclohexene ($2 \vee 2' \vee \overleftarrow{3}$). In addition, as an absolutely necessary step, the scheme must include the desorption of cyclohexene ($\overleftarrow{1'}$) connected by the $\wedge$ operation.

If one starts with pure $D_2$ and deuterium-free cyclohexene, one can obtain deuterium-free cyclohexane ($\uparrow I_6$) only if H–D exchange step $2'$ is connected by the $\wedge$ operation to the steps required by information $\uparrow I_1$ since this provides a route for the formation of the semihydrogenated product with zero deuterium content. Also step $\overrightarrow{4}$ should be omitted and step $\overrightarrow{5}$ must be included as absolutely necessary ($\wedge$ operation).

Deuteration of light cyclohexene can result in the formation of cyclohexane containing more than 2 deuterium atoms ($\uparrow I_7$) only if one of the steps leading to H–D exchange ($2 \vee 2' \vee 2'' \vee \overleftarrow{3}$) is connected by the $\wedge$ operation to the steps required by the $\uparrow I_1$ information.

Information $\uparrow I_8$ means that the concentration of the cyclohexane fraction with more than 2 deuterium atoms is approximately proportional to the deuterium pressure. In order to interpret this, step $\overrightarrow{5}$ should be omitted from $\uparrow I_1$ but, as an absolutely necessary element, step $\overrightarrow{4}$ must be included through the $\wedge$ operation.

According to Table 1, the individual pieces of experimental information assume the following values:

$$I_1 = I_3 = I_5 = I_6 = I_7 = I_8 = \uparrow; \quad I_2 = I_4 = \downarrow. \qquad (9)$$

On the basis of expression (9) and Table 2, the following solution is obtained for the "system of Eqs. (1–8)":

$$\overrightarrow{1} = \overleftarrow{1} = \overrightarrow{1'} = \overleftarrow{1'} = \overleftarrow{1''} = 2' = \overrightarrow{3} = \overrightarrow{4} = \overrightarrow{5} = \uparrow,$$
$$2 = \overleftarrow{3} = \downarrow, \qquad (10)$$
$$\overrightarrow{1''} \wedge 2'' = \downarrow.$$

Thus, in order to interpret the available experimental information, it is necessary and sufficient to regard steps $\overrightarrow{1}$, $\overleftarrow{1}$, $\overrightarrow{1'}$, $\overleftarrow{1'}$, $\overleftarrow{1''}$, $2'$, $\overrightarrow{3}$, $\overrightarrow{4}$, and $\overrightarrow{5}$ shown in Fig. 1 as participating and steps 2 and $\overleftarrow{3}$ as not-participating. It was not possible to arrive at unequivocal conclusions about steps $\overrightarrow{1''}$ and $2''$. We know only that one or both should be regarded as not-participating steps.

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