KINETIC STUDY OF HETEROGENEOUS CATALYTIC REACTIONS OF CONVERSION OF HYDROCARBONS

THESIS

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Kinetic Study of Heterogeneous Catalytic Reactions Of Conversion of Hydrocarbons.

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NOTE

Beside the work carried out in this thesis, the candidate has attended post graduate courses for one year in physical chemistry covering the following topics:

1. Advanced surface chemistry.
2. Advanced electrochemistry and corrosion.
3. Photo chemistry.
4. Quantum chemistry.
5. Instrumental analysis.
6. Thermodynamics.
7. Kinetic and reaction mechanism.

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CHAPTER I

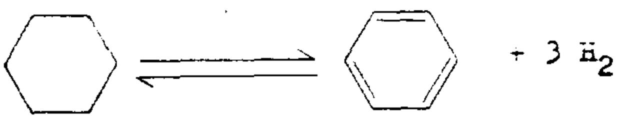
INTRODUCTION

I.A. The mechanism of heterogeneous catalytic dehydrogenation of cyclohexene:

One of the essential problems in chemistry is the elucidation of reaction mechanisms by means of the undisturbed analysis, and through the description of the reaction intermediates. In the recent years, however, new techniques have lead to conceivable principles which permit a reaction to be described as a "radical mechanism" or a "carbonium ion mechanism". These classifications are still insufficient for predicting catalytic systems. A more detailed explaination of surface reactions is still far from being complete, and the prediction of catalytic mechanisms in terms of molecular action faces numerous uncertainties. Evidently, reaction intermediates are described primarily as chemical entities with definite chemical composition. Moreover, the degree of intramolecular excitation and the behaviour of molecular energy exchange as an intermolecular property are decisive. Since these fundamental questions of excitation are generally unknown evenfor homogeneous reactions, investigations in heterogeneous catalysis have first to be restricted to simple structural problems of intermediate compositions.

The dehydrogenation of cyclohexane (I) is one of the catalytic reactions with numerous contradictory statements.

Dehydrogenation catalysts are, in principle, the metals of Group VIII in the periodic table, copper oxides and sulphides of metals which are active in hydrogenation reactions. It is known that the dehydrogenation process takes place at a temperature higher than that of hydrogenation. The catalysts of dehydrogenation are prepared by such methods to be active at a temperature range of 400°C-500°C(1).



cyclohexane (I)   benzene (IV)

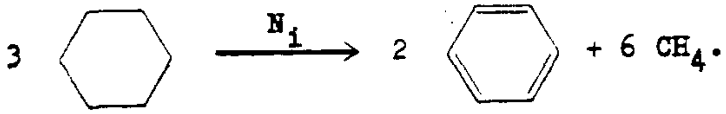
Since dehydrogenation reactions are endothermic reactions, then the decrease of pressure and increase of temperature should accelerate the rate of dehydrogenation reactions.

The first study of catalytic dehydrogenation was discussed by Berthelot(2) in (1866) and by Sabatier et al.(3) in (1897), on studying aliphatic compounds:

$$n\ HC \equiv CH \xrightarrow{Fe} C_{2n} + nH_2\ ;$$

$$H_2C = CH_2 \xrightarrow{Ni} HC \equiv CH + H_2.$$

The catalytic dehydrogenation of six-membered cyclic hydrocarbons using various catalysts, was discussed, by Zelinskii(4,5). On studying the dehydrogenation of cyclohexane over nickel catalyst, Zelinskii proposed the dissociation of C-C bond besides the dehydrogenation reaction:-



I IV

However, the conversion of cyclohexane was studied on nickel/glinsa catalyst at 330-350°C by Zelinskii(5,6) and Shuiken(6,7). The products were benzene, methane, toluene, Xylene, methyl cyclohexane and dimethylcyclohexane, Zelinskii and Shuiken(6,7) proposed the formation of methylene radicals among the intermediate compounds, and gave the following reaction scheme:-

$$1.\ C_6H_{12} \longrightarrow \begin{cases} C_6H_6 + 3H_2 \\ 6\ CH_2\ ; \end{cases}$$

$$2.\ CH_2 + H_2 \longrightarrow CH_4;$$

$$3.\ C_6H_6 + CH_2 \longrightarrow C_6H_5 - CH_3;$$

$$4.\ C_6H_6 + 2CH_2 \longrightarrow C_6H_4 - (CH_3)_2\ ;$$

$$5.\ C_6H_{12} + CH_2 \longrightarrow C_6H_{11} - CH_3\ ;$$

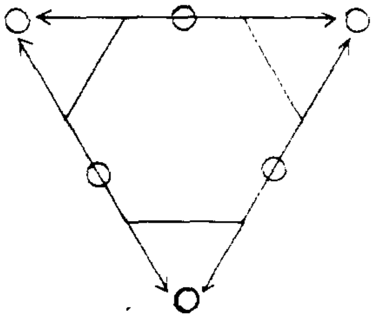
$$6.\ C_6H_{12} + 2CH_2 \longrightarrow C_6H_{10} - (CH_3)_2\ .$$

Nowadays, the radical mechanism is supported by Kiperman et al(8-10).

According to the multiplet theory of heterogeneous catalysis proposed by Balandin(11-20), the dehydrogenation reactions contain in their index two hydrogen atoms. Besides, the index contains one more horizontal bond (which passes into a double bond during the reaction). The reaction is monomolecular and therefore more convenient for kinetic measurements. In the doublet mechanism dehydrogenation of alcohols, amines and hydrocarbons, the indices are accordingly equal:

$$\begin{array}{ccc} C & - & O \\ | & & | \\ H & & H \end{array} \quad ; \quad \begin{array}{ccc} C & - & N \\ | & & | \\ H & & H \end{array} \quad ; \quad \begin{array}{ccc} C & - & C \\ | & & | \\ H & & H \end{array} \quad .$$

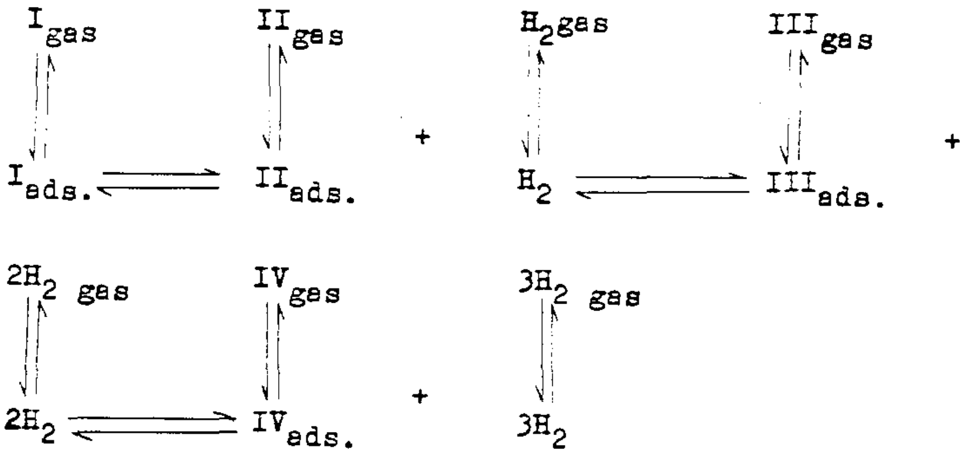
The multiplet theory(11-20) first gave the sextet model of the dehydrogenation of cyclohexane and its derivatives. The reaction takes place nearly at 300°C on metal catalysts. The transitions of hydrogen atoms are shown by arrows in the following Figure.



There is a correspondence between elements of symmetry of the molecule and the catalyst. A six membered ring is superimposed flatly on the (III) face. The atoms of the latter are arranged in the manner of equilateral triangles. The common basis of these discussions was the absence of intermediates like cyclohexene (II) and cyclohexadiene (III). The reacting molecule (I) was postulated to split the six hydrogen atoms after just one adsorption step. Benzene and hydrogen remain, then, as the only desorbing reaction products.

Another indirect argument requiring intermediates is connected with isomerization reactions which are observed during the dehydrogenation of naphthenes$^{(21)}$. Carbonium ions, as the intermediates of these isomerization reactions, are easily formed by olefin traces.

Block$^{(22)}$ proposed the following general scheme of dehydrogenation of cyclohexane.



If follows from this scheme that the dehydrogenation of cyclohexane (I) proceeds by forming the intermediates: cyclohexene (II) and cyclohexadiene (III). Moreover, ionic radicals which are explained by the half-hydrogenated state of adsorbed hydrocarbons are found.

Richardson et al.(23) studied the dehydrogenation of cyclohexane in a flow reactor on a number of oxide catalysts. Rate constants and apparent activation energies were determined in the temperature range 400-465°C. It was shown that the reaction is essentially first order with respect to cyclohexane pressure. Comparison of the rate constants at 450°C for the studied oxides indicates that the catalytic activity is determined by the 3d electron configuration of the metal ion. The results support the application of crystal field theory to the formation of surface complexes. This point of view is previously given by Jermen(24) and Krilov(25).

Horescu and Rudenko(26) discussed the kinetics of dehydrogenation of cyclohexane and methyl-cyclohexane on Pt/C catalyst using a flow technique with the variation of the pressure from 700 mm Hg to 70 mm Hg. They found that the speed of dehydrogenation of methylcyclohexane was decreased 9 times, while that of cyclohexane was not affected by lowering the total pressure. They suggested that the dehydrogenation reaction takes place via the formation of polymolecular catalytic complex. This complex is formed owing to the condensation products on the catalyst surface. The limiting stage is the formation of this polymolecular catalytic complex.

The role of Pt/alumina and Pd/alumina catalysts in the dehydrogenation of cyclohexane were studied by Maatman et al (27,28). It was shown that the reaction is much more complicated and the results are consistent with the evidence that cyclohexene is a necessary intermediate. The degradation-dehydrogenation mechanism was supported also by Hishida et al (29) and Gland et al (30).

It should be mentioned that in all the cases of stepwise dehydrogenation (31), a doublet mechanism (edgewise orientation) takes place, as in the already given study by multiplet theory.