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AN ATTEMPT OF QUANTUM MECHANICAL INTERPRETATION OF REACTIONS OF ISOBUTANE IN THE PRESENCE OF SOLID CATALYSTS

By

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Abstract

The energies of hydrocarbons, ions and radicals which can be formed as a result of isobutane reactions have been calculated by the CNDO/2 method. On this basis the energy changes accompanying hypothetical isobutane decomposition processes have been evaluated. The energy changes were regarded as the criterion of probability of occurrence of the decomposition processes.

The results of the calculations indicate that the formation of carbanions and radicals is most probable. This conclusion does not exclude the probability of formation of carbocations,since it can be formed as a result of interactions of the radicals with the positively charged fragments (acidic centre).

The present work represents the first attempts of interpretation of the model interactions between a hydrocarbon and an active centre.

In the previous communication[1] we reported the results of studies on adsorption and reactions of isobutane in the presence of silica gels containing sodium ions at 300-550°C.

In these conditions isobutane was degraded to methane and propylene and was dehydrogenated to isobutylene and hydrogen. The degradation was the predominant reaction.

Studies on adsorption of isobutane and isobutylene showed that at 400°C the amounts of adsorbed saturated hydrocarbon are similar to those of the unsaturated one. However it should be mentioned that the adsorption was taking place in hydrogen atmosphere which can modify the surface of the catalyst.

Summing up the results of our studies, we have concluded that the amounts of adsorded hydrocarbons and those undergoing the degradation

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do not depend in a simple way on the amount of sodium ions introduced to the catalyst, but largely depend on the amount of water and hydroxylic groups present in the catalyst and on the ratio of sodium content to water content.

In other words the processes taking place on the surface of the investigated gels depend on the ratio of acidic to basic centres, although the existence of radical or ionic-radical reactions cannot be excluded. In our opinion the dehydrogenation reaction takes place according to a free radical mechanism.

All the experimental facts emphasize the complex character of reactions taking place on the surfaces of the investigated gels.

In the concluding part of our previous communication[1], we have proposed a mechanism of the surface reaction in which we assumed that the cleavage of proton from the hydrocarbon molecule is the first stage. In our opinion a polycentric mechanism in which the molecule reacts with several active centres, is more probable.

It is very difficult or perhaps even impossible to prove the validity of such mechanism since it would require the knowledge of energies of various isolated parts of the surface and of the reacting molecule, as well as the energies of the possible transitional complexes and the products (ions and radicals) and the energy of modified fragments of the surface. Also the charge distribution in all the considered fragments of the surface and the molecule would be of interest. These problems could be solved by means of modern quantum chemistry methods which make it possible to calculate approximate energies and related properties of molecules of hydrocarbons and their derivatives. In heterogeneous catalysis, the surface of a solid is one of the reagents. This fact presents the problem of obtaining an objective description of active centres of the catalytic surface.

It is well known that surfaces of solids contain various active centres and that various interactions are possible between the neighbouring centres. At the present time the existing techniques of calculations do not make it possible to describe mathematically large fragments of surface of a catalyst is such a way that all the surface atoms accessible for the approaching molecule are taken into account.

In our interpretation, the catalytically active fragment of surface consists of several atoms accessible for the approaching molecule. For simplicity we assume that the considered fragment does not interact with the bulk of the solid. The presence of a large number of various active centres makes it necessary to take into account all the possible centres. This pro-

cedure could be called the discussion of model interactions of separate fragments of the surface.

In the present work, we give the results of calculations of energy changes in isobutane molecule or its fragments, which can take place during adsorption or a catalytic reaction on the surface of a solid.

We assumed that the criterion of probability of occurrence of a process is the difference between the energy of the products and that of the substrates according to the equation:

$$A+B \longrightarrow C+D, \quad \Delta E=(E_C+E_D)-(E_A+E_B).$$

Negative value of ΔE means that the process is exothermic, and positive that it is endothermic. It is obvious that the value of ΔE calculated in this way has nothing in common with the activation energy of the process.

In order to define the criterion of probability of occurrence of various possible reactions of isobutane it is necessary to know the value of energy E_I of relevant molecules and their fragments. All the values of this energy occurring in this work are collected in Tabel I. They were obtained by CNDO/2[2,3,4] quantum calculations method. The results of the calculations are only approximate, but they are adequate for comparison of energy changes accompanying the considered reactions.

In many published papers the CNDO/2 method has been used for calculation of such quantities as dipole moment[5,6], distribution of charge density[5], ionization potential[5], energy of electronic transitions[5,7,10] and molecular interactions[9]. Thus D. FIELD[8] calculated by the CNDO/2 method the energies of various carbanions such as CH_5^-, CH_3^- and $C_2H_5^-$. H. KOLLMAR and H. O. SMITH[11] used the same method for the theoretical treatment of the energy of CH_5 system in various symmetry states and compared it with the energy of free CH_3^- and H_2.

The quantum chemistry methods are also used for description of hypothetical processes causing effects that are not possible to measure. Thus, J. J. C. HULDER and J. S. WRIGHT[12] investigated by this method the problem of energy states of molecular fragments such as CH_5^-, CH_5^+, and CH_5^- obtained by reactions of methane with H^+ or H^- or by reactions of CH_3^- or CH_3^+ with H_2. The affinity of methane to proton was investigated by KOLLMAR and RUTLEDGE[11,13]. J. A. POPLE[14] investigated reactions of methane with cyclopropane, allene and propylene and obtained theoretical energy differences which were in a good agreement with experimental data.

The above mentioned calculations were carried out by the al intio method. In the RITCHE's work[1,], hypothetical interactions of hydride anion

with water, ammonia and methane are discussed.

Calculations

In order to calculate the difference between the energy of the products and that of the substrates it is necessary to calculate the energies of molecules and ions occurring in the considered processes.

TABLE I

Molecule	Energy (a.u.)	Molecule	Energy (a.u.)
H	− 0.500	$C_3H_5^-$	− 24.753
H_2O	− 19.868	$C_3H_5^\bullet$	− 24.644
OH^-	− 18.908	$C_3H_7^+$	− 26.032
H_3O^+	− 20.242	$C_3H_7^-$	− 26.441
H^-	− 0.477	C_3H_7	− 26.358
H_2	− 1.128	i-C_4H_8	− 34.442
CH_4	− 10.113	i-$C_4H_9^+$	− 34.757
CH_3^+	− 8.669	i-$C_4H_9^-$	− 35 144
CH_3^-	− 9.072	i-$C_4H_9^\bullet$	− 35.051
$CH_3^\bullet$	− 9.081	i-C_4H_{10}	− 36.079
C_3H_6	− 25.716		
$C_3H_5^+$	− 24.252		

The energy values shown in Table I represent the sums of electronic energy and nuclear energy of the molecules. The calculations were carried out for definite bond angles or bond angles and bond lengths. This does not lead to considerable errors, since the bond angles and bond lengths calculated by the CNDO/2 method are in a good agreement with the observed values.

The bond angles and bond lengths used in the calculations are shown in Table II.

TABLE II

Bond lengths		bond angles
C-C par.	1.54 A	109°28′ for sp^3 carbons
C=C ol.	1.34 A	120°00′ for sp^2 carbons and H_3O^+
C-H	1.09 A	109°14′ for H_2O molecule
O-H	1.00 A	

As a result of the calculations the energy values were obtained for neutral molecules, anions and cations. The energies of radicals were calculated from the equation

$$E_R = \frac{E_{R1} + E_{R2}}{2},$$

where

$E_{R1} = E_{cc} + E_{(n+1)c}$; E_{cc} = energy of carbonium ions

$E_{R2} = E_{cA} - E_{(n)cA}$; E_{cA} = energy of carbanion

$E_{(n+1)cc}$ = energy of the first unoccupied molecular orbital in the carbonium ion.

$E_{(n)cA}$ = energy of the highest occupied molecular orbital in the carbanion.

The results of the calculations were used in further treatment of our problem.

We calculated the energy changes accompanying proton, hydride anion and atomic hydrogen cleavage from isobutane molecule.

$$\text{i-}C_4H_{10} \longrightarrow \text{i-}C_4H_9^+ + H^- \qquad (1)$$

$$\text{i-}C_4H_{10} \longrightarrow \text{i-}C_4H_9^- + H^+ \qquad (2)$$

$$\text{i-}C_4H_{10} \longrightarrow \text{i-}C_4H_9^{\bullet} + H^{\bullet}. \qquad (3)$$

This is accompanied by the following energy changes:

$\Delta E_1 = +0.845$ a.u. (22.98 eV)

$\Delta E_2 = +0.935$ a.u. (25.43 eV)

$\Delta E_3 = +0.528$ a.u. (14.36 eV)

The above examples show that the homolytic rupture of the C–H bond is most probable. In the case of the gas phase reactions carried out at elevated temperatures the hydrocarbon molecules react with solid catalyst and with other molecules, atoms or fragments which are present in the gas phase. For this reason in the next stage of our work we were considering hypothetical reactions of isobutane with hydrogen and its ionic forms.

$$\text{i-}C_4H_{10} + H^+ \longrightarrow \text{i-}C_4H_9^+ + H_2 \qquad (4)$$

$$\text{i-}C_4H_{10} + H^- \longrightarrow \text{i-}C_4H_9^- + H_2 \qquad (5)$$

$$\text{i-}C_4H_{10} + H^{\bullet} \longrightarrow \text{i-}C_4H_9^{\bullet} + H_2 \qquad (6)$$

This is accompanied by the following energy changes ΔE:

$\Delta E_4 = +0.194$ a.u. $(5.27\ eV)$

$\Delta E_5 = -0.193$ a.u. $(-5.25\ eV)$

$\Delta E_6 = -0.100$ a.u. $(-2.72\ eV)$.

Energetic transformations 4, 5 and 6 clearly differ from transformations 1, 2 and 3. In the former case the role of acceptor of hydrogen and its ionic forms is very pronounced and low ΔE values are due to the stability of the resulting hydrogen molecule. It should be pointed out that the presence of such forms as $H^{\cdot}$, H^{-} and H^{+} on the surface of the catalyst is very improbable, but they can be regarded as the first approximation of ionic and radical centres of the surface.

The catalyst investigated in the present work were mainly metal oxides. In addition to lattice oxygen the surfaces of these catalysts contained other molecules containing oxygen, such as water, which is strongly bonded to the majority of crystalline or amorphous oxides, and hydroxy groups.

It was of interest to find out how hydrocarbon molecules react with the oxygen containing fragments.

$$\text{i-}C_4H_{10} + H_2O \longrightarrow \text{i-}C_4H_9^{+} + H_2 + OH^{-} \qquad (7)$$

$$\text{i-}C_4H_{10} + H_3O^{+} \longrightarrow \text{i-}C_4H_9^{+} + H_2 + H_2O \qquad (8)$$

$$\text{i-}C_4H_{10} + OH^{-} \longrightarrow \text{i-}C_4H_9^{-} + H_2O. \qquad (9)$$

These reactions correspond to the following energy changes:

$E_7 = +1.154$ a.u. $(31.39\ eV)$

$E_8 = +0.568$ a.u. $(15.45\ eV)$

$E_9 = +0.075$ a.u. $(2.04\ eV)$.

Examples 7–9 (indicate that irrespectively of the absolute values) the formation of the carbanions should take place the most readily as a result of contacts of the hydrocarbon molecules with OH^{-} groups; reaction (8) is energetically more probable than reaction (7).

The examples of hypothetical reactions considered in the present work suggest that carbanions and radicals are preferentially formed. This conclusion offers a corroboration of our hypothesis postulated in the previous paper, but it contradicts the existing opinions.

The question arises whether carbonium ion can be formed during the reaction and what could be the pathway of their formation. For this reason in the next stage of our work we were considering the possibility

of transformations of various ions and radicals into each other according to equations (10–12).

$$i\text{-}C_4H_9^{\bullet} + H^+ \longrightarrow i\text{-}C_4H_9^+ + H \tag{10}$$

$$i\text{-}C_4H_9^{\bullet} + H^- \longrightarrow i\text{-}C_4H_9^- + H \tag{11}$$

$$i\text{-}C_4H_9^{\bullet} + H_3O^+ \longrightarrow i\text{-}C_4H_9^+ + H_2O + H \tag{12}$$

$E_{10} = -0.206$ a.u. $(-5.60\ eV)$

$E_{11} = -0.116$ a.u. $(-3.16\ eV)$

$E_{12} = -0.068$ a.u. $(1.85\ eV)$.

The above examples show that the formation of carbonium ions is possible as a result of interactions of radicals with suitable fragments of the surface.

Comparison of the energies of various hypothetical reactions described in the present work leads to the conclusion that the formation of carbanions and free radicals is favored from the point of view of energy changes. Obviously the reactions considered here are only a part of transformations taking place during the catalytic process. The energy rich fragments formed during this process can react with each other or with fragments of the surface and such reactions can alter the overall picture of energy changes. Nevertheless in our opinion the results of the present work lead to the conclusion that the formation of carbonium ions from hydrocarbons is the least probable of the considered reactions.

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