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

By

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Abstract

The possible pathways of decomposition of hypothetical carbocation, carbanion and radical formed during the decomposition of isobutane are discussed as well as the spontaneous decomposition of isobutane to cracking products involving the rapture of carbon-carbon bonds.

It was found that in the spontaneous decomposition of isobutane the proton cleavage leading to the formation of an ion or a radical takes place more readily than the rupture of a carban-carbon bond.

The results of theoretical treatment of possible pathways of decomposition of the hypothetical carbocation, carboanion and radical indicate that the formation of cracking products, such as methane and propylene, should take place more readily than that of other products. This conclusion is in agreement with results of experimental studies on this problem.

In the previous communication[1] we have reported the results of quantum mechanical calculations for hypothetical reactions of decomposition of isobutane. We have discussed the possibility of formation of carbocations, carbanions and free radicals ($C_4H_9^+$, $C_4H_9^-$ and $C_4H_9\cdot$) and we have reached the conclusion that the formation of carbanions or free radicals is the most probable.

All the hypothetical reactions of isobutane discussed in the previous work[1] were limited to the formation of ionic or radical forms after the cleavage of a proton, a hydride anion or a hydrogen atom (H^+, H^- or $H\cdot$) from isobutane molecule, *i.e.* after the rupture of a carbon-hydrogen bond.

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In the present work we are presenting the results of quantum mechanical calculations for isobutane reactions in which the rupture of a carbon-carbon bond takes place, such as:

1. $i\text{-}C_4H_{10} \longrightarrow CH_3^+ + C_3H_7^-$
2. $i\text{-}C_4H_{10} \longrightarrow CH_3^- + C_3H_7^+$
3. $i\text{-}C_4H_{10} \longrightarrow CH_3\cdot + C_3H_7\cdot$

These reactions are accompanied by the following energy changes:

$\Delta E_1 = +0.969$ a.u. (26.375 eV)

$\Delta E_2 = +0.975$ a.u. (25.520 eV)

$\Delta E_3 = +0.640$ a.u. (17.408 eV).

These energies are higher than those corresponding to the cleavage of a carbon-hydrogen bond. The homolytic cleavage requires the lowest energy.

The possibility of reactions of isobutane molecules with protons, hydride anions and free radicals during catalytic processes should be also considered:

4. $i\text{-}C_4H_{10} + H^+ \longrightarrow CH_4 + C_3H_7^+$
5. $i\text{-}C_4H_{10} + H^- \longrightarrow CH_4 + C_3H_7^-$
6. $i\text{-}C_4H_{10} + H\cdot \longrightarrow CH_4 + C_3H_7\cdot$

These reactions are accompanied by the following energy changes:

$\Delta E_4 = -0.066$ a.u. (-1.795 eV)

$\Delta E_5 = +0.002$ a.u. (0.054 eV)

$\Delta E_6 = +0.108$ a.u. (2.938 eV).

The formation of the cation should take place the most readily and that of the free radical the least readily. This result differs from the conclusion obtained in the previous work[1] according to which the formation of the carbanion ($i\text{-}C_4H_9^-$) should take place the most readily and that of the carbocation ($i\text{-}C_4H_9^+$) the least readily. However, the general conclusion is that the cleavage of a carbon-hydrogen bond should take place more readily than that of a carbon-carbon bond.

Decomposition of isobutane fragments

For the above reasons the investigation of the reactions leading to the formation of methane, propylene, isobutylene and hydrogen was of interest.

Such products can be formed as a result of further decomposition of isobutane fragments.

We have first considered carbon-carbon bond cleavage in the carbocation, carbanion and radical not involving reactions with other molecules. In this case methane is the only stable product:

7. $i\text{-}C_4H_9^+ \longrightarrow CH_4 + C_3H_5^+$

8. $i\text{-}C_4H_9^- \longrightarrow CH_4 + C_3H_5^-$

9. $i\text{-}C_4H_9\cdot \longrightarrow CH_4 + C_3H_5\cdot$

The accompanying energy changes are as follows:

$\Delta E_7 = +0.392$ a.u. (10.662 eV)

$\Delta E_8 = +0.278$ a.u. (7.562 eV)

$\Delta E_9 = +0.294$ a.u. (7.997 eV).

These energies are much lower than those accompanying reactions 1–3, but higher than those calculated for reactions 4–6.

The reactions leading to the formation of propylene as one of the stable products are similar:

10. $i\text{-}C_4H_9^+ \longrightarrow CH_3^+ + C_3H_6$

11. $i\text{-}C_4H_9^- \longrightarrow CH_3^- + C_3H_6$

12. $i\text{-}C_4H_9\cdot \longrightarrow CH_3\cdot + C_3H_6$

The accompanying energy changes are:

$\Delta E_{10} = +0.372$ a.u. (10.118 eV)

$\Delta E_{11} = +0.356$ a.u. (9.683 eV)

$\Delta E_{12} = +0.254$ a.u. (6.909 eV)

In general this pathway of formation of methane and propylene requires a high energy.

Let us now discuss the simple decomposition of the intermediate compounds to isobutylene:

13. $i\text{-}C_4H_9^+ \longrightarrow i\text{-}C_4H_8 + H^+$

14. $i\text{-}C_4H_9^- \longrightarrow i\text{-}C_4H_8 + H^-$

15. $i\text{-}C_4H_9\cdot \longrightarrow i\text{-}C_4H_8 + H\cdot$

$\Delta E_{13} = +0.315$ a.u. (8.568 eV)

$\Delta E_{14} = +0.225$ a.u. (6.120 eV)

$\Delta E_{15} = +0.109$ a.u. (2.965 eV)

By comparing the energies of reactions 7–15 it can be seen that reaction 15 leading to isobtylene formation is favoured.

Considering reactions 13–15 we come to the conclusion that olefins are good acceptors of ions and free radicals.

Since it could be expected that ions and radicals would facilitate the decomposition of the intermediate products we have considered hypothetical reactions involving H^+, H^-, H_3O^+ and H. The presence of such fragments on real catalytic surfaces is rather doubtful, but by assuming their existence it is easier to understand the activity of the active centres of oxide catalysts.

Let us first consider the reactions involving hydrogen cleavage:

16. $i\text{-}C_4H_9^+ + H^- \longrightarrow i\text{-}C_4H_8 + H_2$

17. $i\text{-}C_4H_9^- + H^+ \longrightarrow i\text{-}C_4H_8 + H_2$

18. $i\text{-}C_4H_9\cdot + H\cdot \longrightarrow i\text{-}C_4H_8 + H_2$

19. $i\text{-}C_4H_9^- + H_3O^+ \longrightarrow i\text{-}C_4H_8 + H_2O + H_2$

$\Delta E_{16} = -0.336$ a.u. (− 9.139 eV)

$\Delta E_{17} = -0.426$ a.u. (−11.587 eV)

$\Delta E_{18} = -0.019$ a.u. (− 0.517 eV)

$\Delta E_{19} = -0.052$ a.u. (− 1.414 eV).

The energies of reactions 16–19 are quite different from those of reactions 13–15 as a result of stabilisation of the system by the formation of hydrogen molecule. It is rather surprising that the favoured reactions involve the isobutylene formation from carbanions and carbocations and not the formation from free radicals.

Let us now consider the reactions leading to the formation of methane and propylene:

20. $i\text{-}C_4H_9^+ + H^- \longrightarrow CH_4 + C_3H_6$

21. $i\text{-}C_4H_9^- + H^+ \longrightarrow CH_4 + C_3H_6$

22. $i\text{-}C_4H_9\cdot + H\cdot \longrightarrow CH_4 + C_3H_6$

23. $i\text{-}C_4H_9^- + H_3O^+ \longrightarrow CH_4 + C_3H_6 + H_2O$

which are accompanied by the following energy changes:

$\Delta E_{20} = -0.595$ a.u. (-16.184 eV)

$\Delta E_{21} = -0.685$ a.u. (-18.632 eV)

$\Delta E_{22} = -0.278$ a.u. (-7.562 eV)

$\Delta E_{23} = -0.311$ a.u. (-8.459 eV).

In this case, as in reactions 16–19, the ionic processes are favoured.

Comparing the reactions of decomposition to methane and propylene with the dehydrogenation reactions we can say that the decomposition should take place more readily. This is in agreement with observed decomposition of isobutane in which the cracking to methane and propylene is the dominant reaction. Using the calculated energy values it is possible to calculate the thermal effects of the competing reactions:

24. $i\text{-}C_4H_{10} \longrightarrow i\text{-}C_4H_8 + H_2$; $\Delta E_{24} = 0.509$ a.u. (13.845 eV)

25. $i\text{-}C_4H_{10} \longrightarrow CH_4 + C_3H_6$; $\Delta E_{25} = 0.250$ a.u. (6.800 eV)

This result clearly shows that the reaction involving the rupture of carbon-carbon bond is favoured.

The ΔE_{24} and ΔE_{25} values obtained by CNDO/2 calculations are in a fairly good agreement with the enthalpy change values obtained for these reactions from the standard data (as regards the $\Delta E_{24}/\Delta E_{25}$ ratio).

It has been found that:

$\Delta H^\circ_{24} = +28.11$ kcal/mole;

$\Delta H^\circ_{25} = +19.15$ kcal/mole.

Hence $\Delta H^\circ_{24}/\Delta H^\circ_{25} = 1.468$, whereas $\Delta E_{24}/\Delta E_{25} = 2.043$.

Conclusions

In the previous paper[1] we have discussed the possibility of formation of isobutyl carbanion, carbocation and radical. The results of our calculations indicate that the carbanion and the free radical should be formed more readily than the carbocation, but the latter can be formed as a result of secondary reactions of the radical.

In the present communication we are discussing the decomposition of intermediate products (carbocation, carbanion and radical) and isobutane itself involving the rupture of a carbon-carbon bond. The results of our calculations indicate that the rupture of a corbon-hydrogen bond leading to the formation of the carbanion or the free radical should take place more

readily than that of the carbon-carbon bond leading to the formation of the corresponding ions.

Analysis of the decomposition of the intermediate products (carbanion, carbocation and radical) leads to the conclusion that the effect of hypothetical active centres is very pronounced and that the presence of such centres considerably increases the probability of occurrence of the decomposition process. In also follows from our discussion that the decomposition of isobutane to methane and propylene should be favoured; this conclusion is in agreement with results of experiments.

Since we regard the present work as a preliminary investigation, we have been using simple atoms and ions, such as H, H^+ H^- and in particular H_3O^+, as models of the active centres. In the previous work[1] we have also discussed hypothetical processes involving OH^- and H_2O.

Our results indicate that reactions involving oxygen containing fragments are energetically much less favoured. On the other hand they correspond more closely to the real active centres.

The calculated energy values should not be compared with experimentally determined energies and can be used only as a criterion of probability of occurrence of various processes.

The above discussed hypothetical processes are regarded as the first step in the analysis of more complex situations which are possible on catalytic surfaces and in which polycentre interactions can take place.

References

1) W. GRABOWSKI and S. MALINOWSKI, This Journal. **21**, 110 (1973).