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# NOTES

## On the Mechanism of Alkane Hydrogenolysis

Selective demethylation of hydrocarbons over Ni catalysts which eliminates $CH_3$ groups exclusively is well known (*1–5*). At the same time the ability of Pt catalysts to disrupt nearly all C–C bonds in alkane molecules is now reliably established (*1*, *4*). With respect to the selectivity in alkane hydrogenolysis other noble metals of Group VIII can be placed between Pt and Ni though in some cases (see, e.g., Ref. (*4*)) they show a behavior similar to Pt. The present report discusses the data obtained with Pt and Ni catalysts since these metals show the most pronounced differences in the rupturing of the specific bonds in hydrocarbon molecules. It was of interest to clarify the question of whether the different selectivity of Pt and Ni catalysts can be related to the preferential coordination of the metal with C atoms of a specific electron density.

Earlier we have suggested that the charges of C atoms and donor (acceptor) properties of the active sites are two principal factors responsible for the orientation of the adsorbed molecule towards the active sites (*6*, *7*). In this work the experimental data (*1–5*) on the selective hydrogenolysis are compared with the electron densities of different C atoms in alkane molecules, which are calculated by a quantum chemical technique.

According to Hoffmann (*8*) the negative charges of C atoms in alkane molecules decrease in the order: primary C > secondary C > tertiary C, whereas the quaternary C bears a positive charge. To make the comparison of the experimental and quantum chemical data more obvious we have calculated the charges of C atoms in the molecules of isomeric hexanes. The method and parameters reported by Hoffmann (*8*) have been used for this calculation. The charges of C atoms in isomeric hexanes and all possible products of hydrogenolysis are shown in Fig. 1.

First we shall compare the data obtained for Ni catalysts. It seems reasonable to postulate that the transformation of alkane molecules to eliminate $CH_3$ groups exclusively may be ascribed to the preferential adsorption of primary C atoms, i.e., the atoms with the highest electron density. Further, $CH_3$ groups bound with the secondary C atoms are removed more easily than those attached to tertiary C atoms. This observation has been made by Haensel and Ipatieff (*2*) in their study of demethylation of various hydrocarbons over a nickel-on-kieselgur catalyst. Similar data were obtained by Kochloefl and Bašant (*5*) when they studied demethylation of 2-methylheptane over $Ni–Al_2O_3$. Therefore the scission of the bond between the primary C and the secondary C which unites carbons with relatively large negative charges is a predominant reaction pathway with Ni–kieselgur and Ni–alumina systems. A different behavior has been reported for $Ni–SiO_2$ catalysts. Matsumoto *et al.* (*1*) have studied demethylation of 2-methylpentane (2-MP) and 3-methylpentane (3-MP) over $Ni–SiO_2$ catalysts and found the ratio of *iso*-$C_5$ to *n*-$C_5$ to

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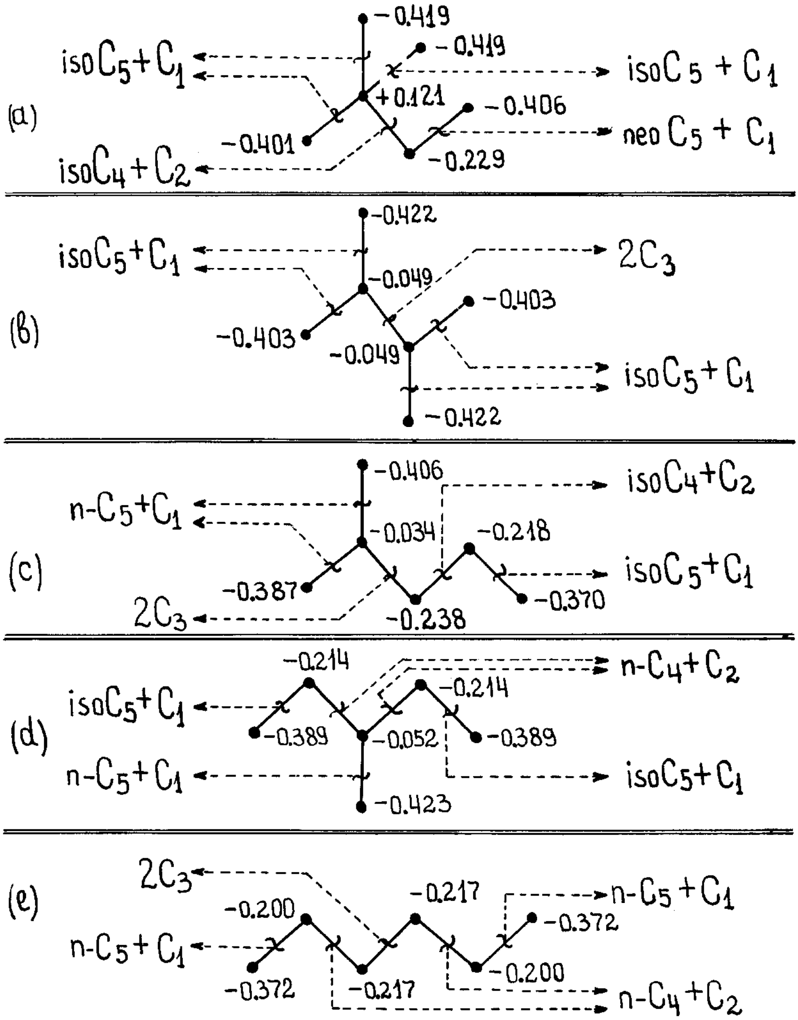


FIG. 1. Effective charges of carbon atoms of isomeric hexanes and products of hydrogenolysis of all five carbon–carbon bonds in each molecule. (a) 2,2-dimethylbutane; (b) 2,3-dimethylbutane; (c) 2-methylpentane; (d) 3-methylpentane; (e) *n*-hexane.

be 1:2 and 2:1, respectively. They explain these ratios by statistical factors. For instance, in the case of 2-MP demethylation, *iso*-$C_5$ is formed following the elimination of the only $CH_3$ group from a secondary C atom while *n*-$C_5$ is formed when one of the two $CH_3$ groups leaves a tertiary C atom (see Fig. 1). With replacement of a silica support by alumina the coordinative power of Ni catalysts toward carbon atoms with an increased electron density becomes more pronounced. As is shown below the same tendency may be traced with Pt catalysts, with alumina taken instead of silica. Moreover, it is well known that upon demethylation of various alkanes with quaternary C atoms over Ni catalysts the cleavage of the bond between these atoms and a $CH_3$ group either occurs at reduced rates (*2*) or is completely suppressed (*1*, *3*). The length of the dative bond in complexes exceeds that of normal covalent bonds (*9*). Therefore it is quite possible to suggest that the dative bond might be formed between a quaternary C atom and a metal

TABLE 1

Isomeric Hexane Hydrogenolysis (*1*)[a]

| Hexane isomer | Catalyst | Product distribution (mole%)[b] | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | $C_1$ | $C_2$ | $C_3$ | *n*-$C_4$ | *iso*-$C_4$ | *n*-$C_5$ | *iso*-$C_5$ | *neo*-$C_5$ |
| 2,2-DMB | Pt-$SiO_2$ | 12.8 | 39.5 | | | 36.9 | | 10.8 | |
| | Pt-$Al_2O_3$ | 26.1 | 24.6 | | | 20.7 | | 28.6 | |
| | Pt-C | 46.9 | | | | | | 53.1 | |
| | Calc.[c] | 40 | 10 | | | 10 | | 30 | 10 |
| 2,3-DMB | Pt-$SiO_2$ | 32.8 | | 37.6 | | | | 29.6 | |
| | Pt-$Al_2O_3$ | 43.3 | | 11.7 | | | | 45.0 | |
| | Pt-C | 48.4 | | 4.4 | | | | 47.2 | |
| | Calc.[c] | 40 | | 20 | | | | 40 | |
| 2-MP | Pt-$SiO_2$ | 22.9 | 10.7 | 30.2 | | 13.3 | 11.7 | 11.2 | |
| | Pt-$Al_2O_3$ | 31.2 | 12.2 | 13.4 | | 11.4 | 16.1 | 15.7 | |
| | Pt-C | 46.9 | 6.7 | 0.9 | 1.5 | 4.5 | 23.1 | 23.4 | |
| | Calc.[c] | 30 | 10 | 20 | | 10 | 20 | 10 | |
| 3-MP | Pt-$SiO_2$ | 25.2 | 25.4 | | 25.1 | | 5.7 | 18.6 | |
| | Pt-$Al_2O_3$ | 35.9 | 10.3 | | 9.1 | | 9.1 | 35.6 | |
| | Pt-C | 47.1 | 2.3 | | 3.1 | | 10.5 | 37.0 | |
| | Calc.[c] | 30 | 20 | | 20 | | 10 | 20 | |
| *n*-H | Pt-$SiO_2$ | 16.6 | 18.7 | 29.1 | 17.6 | | 18.0 | | |
| | Pt-$Al_2O_3$ | 18.8 | 16.9 | 30.6 | 15.5 | | 18.2 | | |
| | Pt-C | 41.1 | 7.2 | 4.5 | 6.6 | | 40.6 | | |
| | Calc.[c] | 20 | 20 | 20 | 20 | | 20 | | |

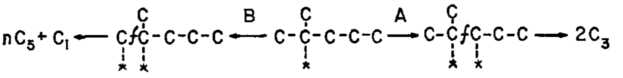
[a] Taken from Ref. (*1*) by permission of the copyright owner.

[b] The experiments with each of the catalyst were performed at constant temperature: Pt-$SiO_2$, 370°C; Pt-$Al_2O_3$, 285°C; Pt-C, 385°C.

[c] The values of the statistical distribution of hydrogenolysis products calculated by the present authors.

atom of the catalyst. Hence the positive charges of the quaternary C atoms play a more important role than steric hindrances preventing Ni atoms in catalysts from effective interaction with these C atoms.

Table 1 shows the data obtained by Matsumoto *et al.* on the distribution of the hydrogenolysis products of isomeric hexanes over Pt–$SiO_2$ (*1*). Also presented are the data on the statistical distribution of hydrogenolysis products which have been calculated by the present authors. By comparing the experimental and calculated values given in Table 1, it is possible to determine the specific C–C bond which is more amenable to disrupture. Further, by comparing these C–C bonds and charges of the corresponding C atoms it may be seen that hydrogenolysis of isomeric hexanes over Pt–$SiO_2$ proceeds with predominant cleavage of the bonds formed by the C atoms with minimum negative charges: quaternary C–secondary C in 2,2-dimethyl/butane (2,2-DMB) to give *iso*-$C_4$ and $C_2$; tertiary C–tertiary C in 2,3-dimethylbutane (2,3-DMB) to give $C_3$; tertiary C–secondary C in 2-MP to give $C_3$; tertiary C–secondary C in 3-MP to give *n*-$C_4$ and $C_2$; secondary C–secondary C in *n*-hexane (*n*-H) to give $C_3$ (cf. Table 1 and Fig. 1). Besides, Table 1 shows that the *iso*-$C_5$ content in the products of 2-MP and 3-MP hydrogenolysis over Pt–$SiO_2$ is almost the same as that calculated, whereas the content of *n*-$C_5$ in the products is considerably lower than the calculated one. The experimental data are, therefore, in apparent disagreement with the regularity described above. For instance, as compared to the calculated values a higher rather than a lower content of *n*-$C_5$ in the product of 2-MP and 3-MP hydrogenolysis could be expected. Normal $C_5$ arises actually as a result of rupture of the bond between tertiary C and primary C, i.e., the bond containing tertiary C with the lowest negative charge. On the other hand, it can be assumed that over Pt–$SiO_2$ the molecule is adsorbed largely by the C atom with the minimum electron density, and the monoadsorbed complex is converted into one of the two 1,2-diadsorbed forms. For example, for 2-MP:



It is evident that direction *A* is prevailing since the electron density of a secondary C atom is considerably lower than that of a primary C atom. For this reason the observed yield of *n*-$C_5$ was relatively low.

From the comparison of Table 1 and Fig. 1 it can also be concluded that on going from Pt–$SiO_2$ to Pt–$Al_2O_3$, and then to Pt–C, a decrease of the relative rates of hydrogenolysis of the bonds between C atoms with a minimum electron density occurs. Kikuchi *et al.* (*4*) have obtained similar results from the study of *n*-pentane hydrogenolysis over Pt–$SiO_2$ and Pt–C catalysts. With Pt the replacement of supports in the series: silica → alumina → charcoal affects the selectivity of the resulting catalysts such that their properties become similar to those of Ni catalysts.

Thus, from the comparison of the experimental data (*1–5*) and the charges of the C atoms we can conclude that alkane hydrogenolysis over Ni catalysts affects primarily the bonds with relatively large negative charges of C atoms, whereas over Pt–$SiO_2$ the bonds in which C atoms have a relatively low electron density are preferred. It may be further speculated that this relation is due to the electron-accepting properties of Ni catalysts and electron-donating properties of Pt–$SiO_2$ with respect to the C atoms in alkane molecules under the conditions of hydrogenolysis.

Finally, let us consider the directions of the two related reactions: hydrogenolysis of isomeric hexanes and methylcyclopentane (MCP) hydrodecyclization which have been studied under the same conditions in Refs. (*1*, *10*). Matsumoto *et al.* (*1*) have demonstrated that unlike alkane hydrogenolysis, MCP hydrodecyclization over Pt–$SiO_2$ proceeds with a preferential cleavage of secondary C–secondary C bonds formed by the C atoms with a maximum electron density in the cycle (cf. (*1*) and (*6*)). We have obtained similar results from the study of MCP hydrodecyclization over Pt–$SiO_2$ (*6*, *7*). Using a thick Pt film instead of an ultrathin one, Anderson and Shimoyama (*10*) have found a considerable increase in the rate of hydrogenolysis of tertiary C–secondary C bonds in 2-MP and 3-MP molecules and, conversely, a sharp decrease in the rate of rupture of these bonds in the MCP ring (*1*). Both reactions seem to involve a 1,2-diadsorbed intermediate but they may be described by different mechanisms. Adsorption of isomeric hexanes as a step of hydrogenolysis does not involve prerupture of C–H bonds (as follows from the above considerations), whereas MCP hydrodecyclization requires prerupture of C–H bonds (*6*, *7*).

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