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LETTER TO THE EDITORS

A π-Complex Mechanism for Catalytic Hydrogenation of the Benzene Ring

Many authors deal with an influence of the electron density in metallic and oxidic catalysts on heterogeneous catalysis. Complementary to this point of view we have investigated the problem of whether the electron density in the substrate, too, has an influence on catalysis or not. The electron density in the benzene ring can be increased by substitution of alkyl groups for hydrogen. Therefore we have studied the catalytic hydrogenation of benzene, toluene, ethylbenzene, *p*-xylene, and mesitylene on an Ni-MgO catalyst.

The publications by Garnett and Sollich (*1*), and Kemball and Rooney (*2, 3*) on the π-complex mechanism for catalytic exchange reactions on cyclic hydrocarbons prompted this preliminary report. A more detailed account of our work and further results will be published very soon.

The hydrogenation reactions being investigated in the vapor phase were performed between 90° and 200°C. The essential result is the following: The activation energy of hydrogenation is decreased in the sequence benzene, toluene, *p*-xylene, ethylbenzene, mesitylene (Table 1). The intersecting points of the corresponding Arrhenius plots are within the temperature range of the measurements. Therefore the sequence of activities inverts depending on the temperature of measuring. So we think that it is of little use to compare the activities and will only discuss the activation energy of hydrogenation.

In the last years there has been a trend in catalysis to interpret catalytic intermediates in terms of complex chemistry (*4*). Kemball and Rooney (*3*) investigated the exchange with deuterium of cycloalkanes and recently proposed a mechanism for various reactions of six-membered cyclic hydrocarbons on metal catalysts involving π-bonded intermediates. Garnett and Sollich (*1*) have studied the exchange between alkylbenzenes and heavy water. They, too, propose a π-complex chemisorbed aromatic hydrocarbon as the first reaction step. Comparing activities and not activation energies, their results are only in an approximate qualitative agreement with the behavior of π-complexes.

TABLE 1
CATALYTIC AND π-COMPLEX PROPERTIES OF ALKYLBENZENES

Substance	Activation energy of hydrogenation [kcal/mole]	Ionization potential[a] [e.v.]	Relative complex stabilities[b]		
			HCl	Picric acid	I_2
Benzene	14.2	9.24	0.66	0.83	0.92
Toluene	13.5	8.82	1.00	1.00	1.00
Ethylbenzene	10.4	8.77	1.15	0.88	—
p-Xylene	11.1	8.44	1.09	1.19	1.92
Mesitylene	8.0	8.39	1.73	1.33	5.10

[a] Reference 8.
[b] Reference 5.

We now find in the sequence of the activation energies that the hydrogenation is facilitated by increasing alkylation. We propose an explanation of this result by comparing the properties of real π-complexes with a proposed formation of intermediate π-complexes in catalysis. In Table 1 are listed the relative stabilities of some π-complexes of the alkylbenzenes (*5*). Generally, the stability increases from benzene to mesitylene complexes. The same trend may be seen in the fact that the chromium complex of mesitylene is formed much easier than the dibenzenechromium (*6*).

In catalysis the easiest hydrogenation is expected in those benzene rings which are most strongly adsorbed, that means, which form the strongest ring metal complex. The lowest activation energy has been found to occur in the mesitylene hydrogenation. This fact is in good agreement with the highest complex stability.

Moreover, complex stability is determined by the ionization potential of the donator molecule (*7*). As the alkyl groups increase the electron density in the benzene ring they lower the ionization potential and promote the formation of a charge-transfer complex. As to be seen in Table 1, the ionization potential (*8*), with one exception only, decreases in the same sequence as the activation energy of hydrogenation. A better agreement is scarcely to be expected. The activation energies usually have a deviation of ±0.5 kcal/mole, and the formation of complexes is not only governed by electronic but also by steric factors.

We see in the same sequence of the activation energy of hydrogenation on the one side and the π-complex stability and the ionization potential on the other side first experimental evidence for π-complex intermediates during catalytic hydrogenation reactions.

Furthermore, by the structure of the π-complexes the question might be answered why the hydrogenation is facilitated. In the lattice of the silver perchlorate-benzene complex the silver ion is located away from the symmetry axis above and between two carbons of the aromatic ring (*9*). Mulliken (*10*) has found an unsymmetrical location of the Cl_2 in the benzene·Cl_2 complex in solution. This asymmetry must interfere with the aromatic π-electron system of the ring. Thus, the olefinic nature of the C–C ring bonds must increase and facilitate the hydrogenation.

To sum up, our results substantiate the following mechanism of the catalytic hydrogenation: The benzene ring acts as a donator and forms a π-complex with a metal atom of the catalyst. Then this complex is successively hydrogenated by adsorbed hydrogen atoms. This mechanism of hydrogenation corresponds with the mechanism proposed by Rooney (*3*) and Garnett and Sollich (*1*) in catalytic deuterium exchange.

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J. VÖLTER

Institut für anorganische Katalyseforschung
der Deutschen Akademie der Wissenschaften
zu Berlin, Berlin-Aldershof

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