# CATALYTIC HYDROGENATION OF BENZENE AND TOLUENE

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## ABSTRACT

The reaction takes Place in liquid phase in a batch reactor, at temperature between 393 K and 433 K. Partial hydrogen pressure is varied between 1.1 MPa and 3.0 MPa. Catalytic activity is expressed in mol of aromatic compund which react per gram of catalyst and per second.

The general mechanism proposed for this kind of reaction assumes that there is no competitive adsorption between the aromatic compound and hydrogen. Reaction occurs between two molecules that are absorbed on two different sites.

The kinetic model which describes the hydrogenation process of aromatic compounds in liquid phase is the following:

$$r_A = \frac{kK_A K_H C_A P_H}{\left(1 + K_A C_A + k_p C_p\right)\left(1 + K_H P_H\right)}$$

Activation energy and adsorption heat increase with the increase of the number of substituents, and with length of the chain in the benzene ring, while reaction velocity decreases.

## INTRODUCTION

The study of aromatic hydrocarbon hydrogenation is of great interest not only due to the commercial use of this reaction, but also due to its utilization in the evaluation of catalysts activity, and in the determination of reaction mechanisms.

From the commercial viewpoint, aromatic hydrocarbon hydrogenation plays a significant role in both the refining and the chemical industries. In refineries the process consists of a total or partial hydrogenation of kerosene cuts, intermediate destillates, paraffin solvents, etc., with the aim of improving their characteristics for subsequent use as fuel, whereas in the chemical industry this process is used to obtain diferent aromatic compounds and their by-products.

Kinetic studies of aromatic compound hydrogenation may provide information for improving hydrogenation processes because they allow us to know tbe variables that affect them. Sometimes, reaction velocity is controlled by the phenomena of material transfer. This implies a variation in activation energy, changes in reation orders as to reactives and modification of selectivity in undesired products. For this effect to be negligible, the kinetic region is determined, which is a state in which reaction velocity is controlled by surface processes.

Most of the works published in this area were carried out with the firts compound of the series, benzene. Few studies have been carried out on toluene and practically nothing has been done on the remaining compounds in the aromatic series. In the case of benzene it has been found that both support and use of acidic oxides considerably increase activity. These results are very promising and interesting to determine the effect that the increase in the length of the aliphatic chain in the benzene ring has upon aromatic compund hydrogenation.

Hydrogenation as a practical process on a large scale has its origins in the works of Sabatier (1900), who found that nonsaturated hydrocarbons may be successfully hydrogenated in the steam phase over a nickel catalyst.

Adsorption and hydrogenation of benzene on metals in group VIII have been the objcct of a lot research. Numerous studies have been carried out using a variety of supports and metals. This reaction has been used to determine the effects of metal-support and the influence of structure over catalytic properties (Chou, 1987; Germain, 1980; Moss, 1979; Yoon, 1983). In recent years, there has been a tendency to study toluene hydrogenation as a reaction which complements studies made on benzene. However, few hydrogenation experiments have been carried out with this aromatic compound and much less with ethylbenzene.

The aim of this work is the study of catalytic hydrogenation of aromatic hydrocarboms in liquid phase, in the presence of a catalyst of Pt/A12O3.

## EXPERIMENTAL SECTION

*Materials*

To guarantee maximum reliability, the utilization of reactives is preceded by purification over rA and 13X molecular screens, to eliminate eventual traces of impurities, such as water and sulfur compounds wich deactivate the catalyst.

The catalyts used is a commercially available one, with a Pt content of 0,35%, supported over alumina.

*Equipment and Methods*

The reaction equipment used in these experiments is made up of a reactor by charges supplied by Autoclave Engineers, with a capacity of 500 cm$^3$, and maximum operating conditions of 2000 psi and 450 ºF. The analysis of reactives and products is carried out by chromatography in gas phase (Mazurka, 1985).

*Data analysis*

The method used to calculate velocity from the aromatic compound concentration with respect to time, consisted of obtaining first a function that matches experimental data, in the most general case of nonlineality. A solution to these problems is that of polynomial least squares. Once the polynomial is obtained through the computer, the concentration derivative in respect of time is nothing but reaction velocity. Determining the specific constants of velocity and adsorption, as well as apparent reaction orders, is made by means of two calculus programs: one based upon the Gauss method, and the other selected as a non-lineal optimization technique, the Box method (Mazurka, 1985).

## RESULTS AND DISCUSSION

*Analysis o f empirical kinetic parameters*

Results obtained for benzene and toluene (Mazurka, 1985a, 1991b) shown in Table 1, demonstrate that experimental data may be adjusted to the empirical model. For every case, apparent reaction orders vary with temperature. The same tendency is obtained by Coughlan (1990), for benzene and toluene; the order regarding the latter is lower. This indicates that toluene is more strongly adsorbed than benzene.

**Table 1.** Empirical Kinetic Parameters

| Aromatic | T (K) | m | n | Ea (kJ/mol) |
|---|---|---|---|---|
| Benzene | 393—423 | 0.406-0.418 | 0.89-0.963 | 24.27 |
| Toluene | 393-423 | 0.10 -0.30 | 0.95-0.80 | 38.40 |

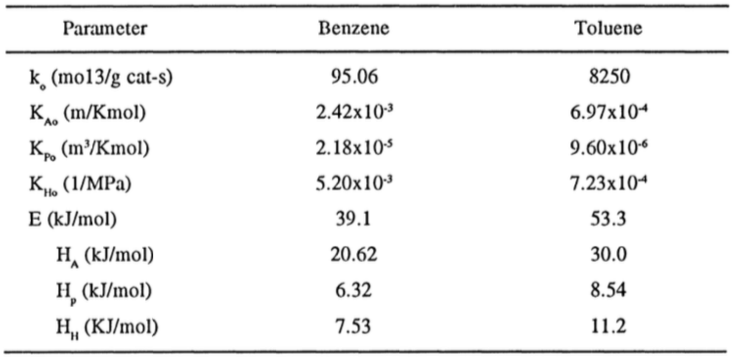
Apparent activation energy increases with the number of substituents, as well as with the length of the chain. The same tendency is observed by Coughlan (1990), who toluene. According to Gudnov (1975), this is so because the substituent $CH_3$ in toluene stabilizes adsorbed *n*, resulting in a higher energy barrier.

On the basis of the empirical kinetic model, it is difficult to explain why orders change with temperature. In this sense, interpretation of these results must be done deriving a kinetic expression for a type of mechanism which adjusts experimental data.

*Analysis of kinetic parameters*

Table 2 shows the values for activation energy, adsorption heat and frequency factors, obtained by adjusting experimental data for benzene and toluene (Mazurka, 1985; 1991). Subindices A, P and H refer to aromatics, products and hydrogen respectively. It can be observed that obtained values are physically acceptable; their magnitude order is within the range reported by literature (Konykhov, 1987; Ross, 1975; Wauquier, 1975) and a decrease in hydrogenation velocity can be established with the increase in the number of substituents (Tsisun, 1981).

**Table 2.** Value of cynetic parameters



| Parameter | Benzene | Toluene |
|---|---|---|
| $k_o$ (mo13/g cat-s) | 95.06 | 8250 |
| $K_{Ao}$ (m/Kmol) | $2.42x10^{-3}$ | $6.97x10^{-4}$ |
| $K_{Po}$ ($m^3$/Kmol) | $2.18x10^{-5}$ | $9.60x10^{-6}$ |
| $K_{Ho}$ (1/MPa) | $5.20x10^{-3}$ | $7.23x10^{-4}$ |
| E (kJ/mol) | 39.1 | 53.3 |
| $H_A$ (kJ/mol) | 20.62 | 30.0 |
| $H_p$ (kJ/mol) | 6.32 | 8.54 |
| $H_H$ (KJ/mol) | 7.53 | 11.2 |

Decrease in reaction velocity has been explained by Gudkov (1975) on the basis of an increase in surface stability ***n*** when the number of substituents over the ring is increased. Tsisun (1981) also observed the same tendency using a catalyst of $Ru/Al_2O_3$. They observed that an increase in the length of the aliphatic chain considerably influences alkyl in hydrogenation velocity:

Benzene > Toluene

## CONCLUSIONS

A kinetic expression was obtained, which represents quite well the aromatic hydrogenation process (benzene and toluene), and is unique in the literature consulted. The values of the kinetic parameters are physically acceptable and consistent with considerations made in the derivation of the model.

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