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Comparative Hydrogenation and Adsorption of Benzene and Methylbenzenes on Cobalt and Rhodium Catalysts

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The hydrogenation of benzene, toluene, *p*-xylene, and mesitylene was studied in the gas phase on rhodium and cobalt supported by magnesium oxide, and the adsorption of these hydrocarbons on the cobalt catalyst by direct weighing. The activity of hydrogenation decreases with increasing number of methyl groups, the strength of adsorption decreases in the opposite sequence.

It is shown that both the adsorption and hydrogenation apparently are governed by a surface π-complex. The activity of hydrogenation, k°, is connected to the coefficients of adsorption and to the relative stabilities K_s of bulk π-complexes with picric acid by linear logarithmic relations.

The results are explained by a model based on the existence of π- and σ-bonded states.

INTRODUCTION

In a previous work we have studied the hydrogenation of benzene, toluene, *p*-xylene, and mesitylene on a Ni catalyst (*1*). We have found a decreasing activity in the above sequence and have proposed an explanation assuming π-complex adsorption of these hydrocarbons with a sequence of strength of adsorption similar to the stabilities of bulk π-complexes. Surface π-complex mechanisms have also been proposed by other authors in hydrogenation (*3*) and in hydrogen exchange (*2*, *3*, *4*). Smith and Campbell (*5*), however, studying the competitive liquid-phase hydrogenation of methylbenzenes on a Rh catalyst have found relative kinetic coefficients of adsorption which exhibit the opposite sequence as expected from π-complex stability. Examining our hypothesis by extension to other metals forming π-complexes, in the present work we studied the gas-phase hydrogenation of benzene, toluene, *p*-xylene, and mesitylene on cobalt and rhodium catalysts supported by magnesium oxide, and also the adsorption of these hydrocarbons on the same cobalt catalyst by direct weighing.

EXPERIMENTAL

The benzenes were hydrogenated in the gas phase successively on the same catalyst in a dynamic apparatus described previously (*1*). The flow rates of hydrogen and hydrocarbons were 2.26 ± 0.04 l hr^{-1} at STP and $(8.15 \pm 0.04) \times 10^{-3}$ mole hr^{-1}, respectively. Hydrogen was deoxygenated by the Gasreinigungskatalysator 7748, VEB Leuna-Werke, and purified from other impurities by trapping with cooled 4 A molecular sieve. The hydrocarbons were purified by carefully fractionating, except mesitylene, which was prepared from its recrystallized sulfonic acid by hydrolysis. Recrystallization was performed three times from 20% hydrochloric acid and once from chloroform.

The catalysts were prepared by a method published previously (*1*) and reduced in hydrogen at 450°C during 5 hr. Metal content by analysis of the reduced catalysts amounts to 3.8 atom % Co and 0.54 atom % Rh. Cobalt catalyst samples of 0.300g, containing 0.0162g Co, and rhodium catalyst samples of 0.200g, containing 0.0026g Rh, were used. The sieved fraction used was 0.200 to 0.315 mm.

Adsorption was measured with a conventional quartz spring McBain balance with a sensitivity of 0.5 mm/mg. Changes in length could be read by a cathetometer to 0.005 mm.

The Co catalyst was reduced by streaming hydrogen in the balance. The conditions of reduction were the same as in the catalytic experiments. After hydrogen treatment outgassing was performed for about 15 hr at 400°C and 10^{-6} torr. The nitrogen BET surface area of the Co catalyst amounts to 7.8 m^2/g.

The hydrocarbons were dried and degassed by vacuum distillation over 4A molecular sieve.

All measurements of adsorption were made at 89°C. Equilibrium was obtained within 20 min. Vapor pressures were calculated from the temperature of the liquid phase of the hydrocarbon in contact with its vapor by the vapor pressure equation. The upper limit of pressures was determined by room temperature. The adsorption was not completely reversible. In consequence, for each adsorption fresh catalyst of the same preparation was reduced.

RESULTS

The catalytic results from the rhodium catalyst are collected in Table 1. Methods of calculation were described previously (*1*). The mean errors of the Arrhenius parameters E and log A are 0.3 kcal/mole and 0.3 for both catalysts. The rate of hydrogenation decreases with increasing number of methyl groups. The apparent energy of activation shows no definite change with number of methyl groups.

The kinetic data of hydrogenation on the cobalt catalyst are listed in Table 2. The rate of hydrogenation also decreases with increasing number of methyl substituents. Compared with rhodium, the activity of cobalt is much less. The activation energy increases definitely with substitution from 11 kcal/mole for benzene to 15 kcal/mole for mesitylene.

The main catalytic result is the decreasing activity with increasing number of methyl groups found for both metals. The same sequence has been found previously on nickel (*1*) and is known from other metals, too (*6*). A general dependence of activation energy on number of methyl substituents, as supposed previously (*1*), obviously does not exist. While with increasing substitution the activation energy of hydrogenation on nickel decreases, on cobalt there is an increase, and on rhodium there is no definite variation.

The adsorption isotherms of the hydrocarbons studied are presented in Fig. 1. It is seen that even at equal relative pressures within the measured range the amount of adsorption increases with the number of methyl groups. For quantitative evaluation the isotherms are plotted according to Langmuir. The resulting plots were approximated by straight lines, from which the coefficients of adsorption b and the monolayer capacities were evaluated. The results are

TABLE 1
RESULTS FROM MEASUREMENTS OF RATE OF HYDROGENATION ON RHODIUM CATALYST[a]

Compound	k_{90}^0 (mole hr^{-1} g^{-1})	E (kcal $mole^{-1}$)	log A	Δt (°C)
Benzene	1.37	9.2	5.7	40–70°
Toluene	0.71	7.4	4.2	45–85°
p-Xylene	0.41	8.7	4.9	65–95°
Mesitylene	0.33	8.0	4.4	87–110°

[a] Rate constant k_{90}^0 at 90°C, activation energy E, frequency factor A, and interval of temperature of measurement Δt.

TABLE 2
RESULTS FROM MEASUREMENTS OF RATE OF HYDROGENATION AND ADSORPTION ON COBALT CATALYST[a]

Compound	$10^2 \times k_{90}^0$ (mole hr^{-1} g^{-1})	E (kcal $mole^{-1}$)	log A	Δt (°C)	b ($torr^{-1}$)	m (μg m^{-2})
Benzene	33.3	11.3	6.3	45–85°	0.026	220
Toluene	15.0	13.1	7.1	55–95°	0.093	252
p-Xylene	9.9	14.2	7.6	65–105°	0.46	221
Mesitylene	1.6	14.9	7.2	90–130°	3.2	254

[a] k_{90}^0, E, A, and Δt as in Table 1, coefficients of adsorption b, and monolayer capacities m.

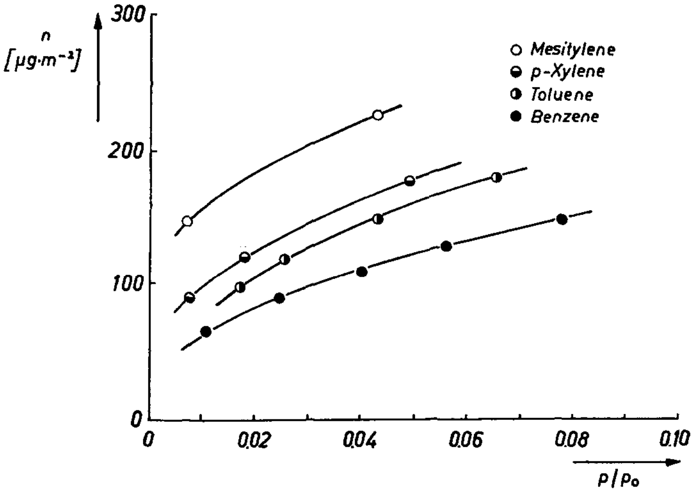

FIG. 1. Adsorption isotherms of benzenes on the Co catalyst at 89°C; p/p_0 is the relative pressure.

shown in Table 2. The strong increase of the coefficients of adsorption with increasing substitution may be represented by a linear logarithmic plot in Fig. 2. The rate of hydrogenation also plotted in this diagram shows an opposite slope. Increasing adsorption is connected with decreasing activity.

The adsorbed amounts per unit area were calculated from the BET nitrogen surface area of the catalyst. No conventional method for measuring metallic surfaces has been used. However, coadsorption of ethylbenzene and oxygen at 200°C, i.e., the oxidation of ethylbenzene to irreversibly adsorbed products, yields a very rapid and high covering of the surface, indicating that the surface is almost completely covered by the active component since pure magnesium oxide is inactive in coadsorption (7).

In one case adsorption was studied in the presence of hydrogen. Only a slight decrease of the amount adsorbed, by a few percent, was observed.

DISCUSSION

Relations between Activity and π-Complex Stability

As has been shown in Fig. 2, the activity of hydrogenation k^0 as well as the directly

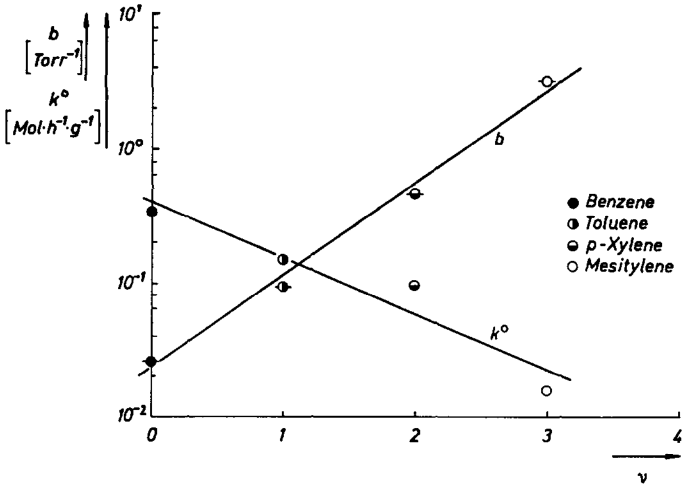

FIG. 2. Dependence of rate constant of hydrogenation $k_{90}{}^0$ and coefficient of adsorption b on the Co catalyst from number ν of methyl groups.

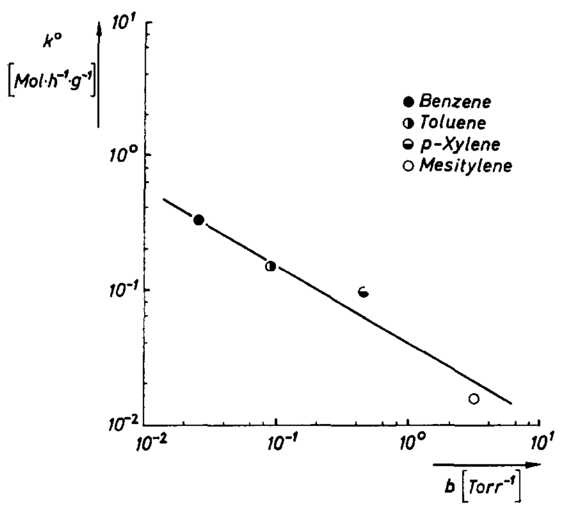

FIG. 3. Relation between rate constant k_{90}^0 and coefficient of adsorption b.

determined coefficients of adsorption b on the cobalt catalyst depend on the number of methyl groups in an opposite manner. Consequently there must be a correlation between activity and strength of adsorption. This is shown in Fig. 3. The relation can be approximated by

$$k^0 = 4.1 \times 10^{-2}\, b^{-0.57} \qquad (1)$$

which is equivalent to a linear free energy relationship. The question arises about the kind of adsorption. The observed dependence of the coefficient of adsorption on the number of methyl groups could also result from pure physical adsorption. However, it has been shown (*8*), that the adsorption of alkylbenzenes even on appropriate oxides (e.g., ZnO) is highly specific by π-complex adsorption (or electron donor–acceptor interaction), as revealed by comparison of the adsorption of benzene and cyclohexane with the same boiling point, whose coefficients of adsorption differ by more than one order of magnitude. Other oxides (e.g., MgO) are less specific in this adsorption. Only those oxides with a high specific adsorption give the strong coadsorption effect and this effect we find on our metal catalysts, too, as mentioned above. Thus we conclude that alkylbenzenes are chemisorbed. The type of bonding should be determined by the π-electrons of the hydrocarbons. This conclusion is supported by our previous investigations (*1*) and by the following relations between b and π-complex stability.

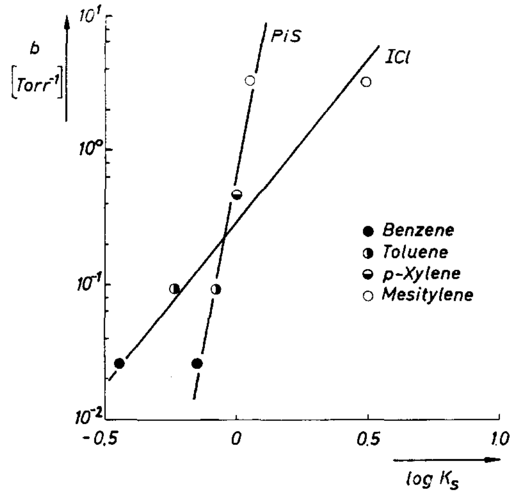

FIG. 4. Relation between coefficients of adsorption b and relative stability constants of π-complexes of methylbenzenes with picric acid and ICl. Values of stabilities from ref. (*9*) p. 148. The point for p-xylene belongs to both lines.

A criterion for π-complexes is their increasing stability with decreasing ionization potential (*1*, *9*). This condition is satisfied by the coefficients of adsorption b. Furthermore between homologous series of π-complexes a symbatic linear free energy relation is in general expected. Two examples of such a relation are shown in Fig. 4 between relative stabilities of π-complexes of methylbenzenes with ICl and picric acid as acceptors and the coefficients of adsorption b. Different slopes result from different strengths of acceptors.

Substituting the relation $b(K_s)$ into $k^0(b)$ we must also arrive at a relation between activity and stability of bulk π-complexes. For simultaneous comparison of different catalysts we have used for this purpose relative rate constants with respect to those of toluene: $k^r = k^0/k_{\text{toluene}}$. The logarithmic plot of k^r versus K_s is shown in Fig. 5. We have used relative stability constants of the picric acid complexes and the relative activities of hydrogenation on Co and Rh studied in this work, on Ni from our former paper (*1*), and on Rh in liquid-phase hydrogenation from Smith and Campbell (*5*). As can be seen from Fig. 5 the four different sets of measurements can fairly be represented by a single straight line expressed by

$$k^r = 0.56\,K_s^{-3.1} \qquad (2)$$

The good fitting also of the activities of Smith and Campbell (*5*) should especially be mentioned, indicating that this relation also holds in liquid-phase hydrogenation. In our opinion, Eq. (2) gives further evidence of a π-complex-governed mechanism of hydrogenation.

A general validity of relation (2) would permit calculation of the activities of hydrogenation for the whole set of hydrocarbons with any catalyst, if the activity for one member of the set for this catalyst is known. The relative activities predicted from the equation of Dyakova and Lozovsky [see ref. (*6*)] also fit fairly the relation (2). However, detailed features of the activity of isomeric compounds will not be predicted by both the relations.

Garnett *et al.* (*4*) have discussed the relative adsorption coefficients of Rader and Smith (*10*), which are similar to those of Smith and Campbell (*5*), in terms of π-complex adsorption. The sequence, opposed to that known from bulk complexes, is interpreted by these authors in terms of steric hindrance to π-adsorption by the substituents. Inspection of known relative stabilities of complexes of alkylbenzenes with acceptors of different bulkiness (*9*, pp. 137 and 148) shows no inversion of the general sequence.

Role of the π-Complex in Hydrogenation

While a connection between catalytic activity, the postulated π-adsorption, and π-complex stabilities with no doubt does exist, the role of the π-complex still remains unexplained. We have the problem of decreasing activity with increasing adsorption. The simple explanation by competitive adsorption of hydrogen and hydrocarbon can be ruled out since such a mechanism would require a negative order with respect to hydrocarbon.

Further, there is the discrepancy with the results of Smith and Campbell (*5*). Their method of competitive reaction for the determination of relative coefficients has been widely used (*11–14*) and agreement between these coefficients and directly measured ones for the oxidation of olefins has been found by Moro-oka and Ozaki (*15*). However, other interpretations of such measurements are possible (*14*). If one accepts the validity of the procedure of Smith and Campbell, one has to clarify the different nature of the coefficients of adsorption. Since these authors have performed their experiments in the liquid phase, their relative kinetic coeffi-

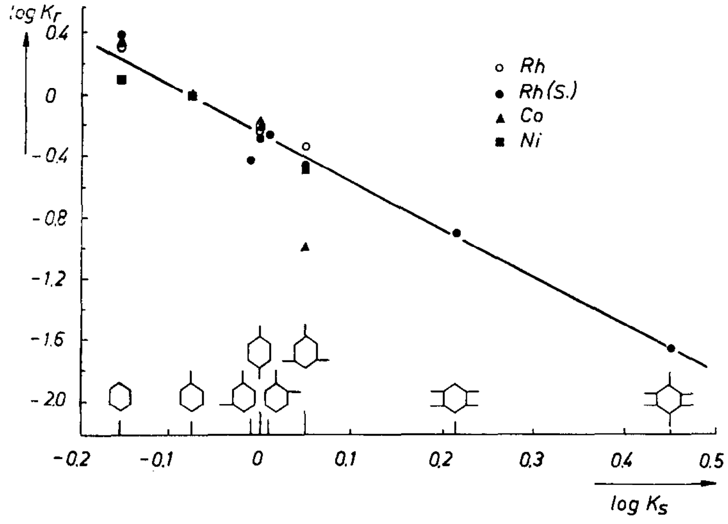

FIG. 5. General relation between rate of hydrogenation and relative stability of π-complexes of methylbenzenes with picric acid. Relative rate for toluene, 1. Rh(S.) Values from Smith and Campbell (*5*).

cients of adsorption are related to the liquid state of the hydrocarbon, whereas the present authors have measured the adsorption from the gas phase. It is very unlikely that the difference in the reference state causes the different sequences of the adsorption coefficients. We assume therefore that the different coefficients of adsorption are related to different adsorbed states, which are related by the following model of hydrogenation.

It is assumed that the hydrogen does not attack the π-adsorbed benzene A_π but a disturbed, reactive state formed from this and denoted by A_σ:

$$A_g + s_\pi \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A_\pi \quad (3a)$$

$$A_\pi + s_\sigma \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} A_\sigma + s_\pi \quad (3b)$$

$$A_\sigma + (H_2) \xrightarrow{k_3} \text{Products} \quad (3c)$$

where A_g is the gaseous benzene and s_π and s_σ are the corresponding adsorption sites. The surface concentrations of the adsorbed species A_π and A_σ are θ and σ, respectively.

The rate may then be given by

$$r = k'_3\sigma\theta_H(p_{H_2}) \quad (4)$$

Assuming no competitive adsorption of hydrogen with the hydrocarbon, and a first order with respect to hydrogen, for simplicity, we have

$$r = k_3\sigma p_{H_2} \quad (5)$$

A steady state treatment (*16*) of (3a)–(3c) with the stationary conditions $d\theta/dt = 0$ $d\sigma/dt = 0$ results in

$$K_2\left(\frac{K_1p - k_3\sigma p_{H_2}}{k_{-1}}\right)(1-\sigma) = \sigma\left(\frac{1 + k_3\sigma p_{H_2}}{k_{-1}}\right) + \frac{k_3\sigma p_{H_2}(1 + K_1p)}{k_{-2}} \quad (6)$$

where $K_1 = k_1/k_{-1}$, $K_2 = k_2/k_{-2}$, and p, the pressure of hydrocarbon. Neglecting the terms with the rate-determining constant k_3 ($k_3 \gg k_1, k_{-1}, k_2, k_{-2}$) yields

$$K_1K_2p(1-\sigma) = \sigma$$

and

$$\sigma = K_1K_2p/(1 + K_1K_2p) \quad (7)$$

or with (5)

$$r = k_3p_{H_2}K_1K_2p/(1 + K_1K_2p) \quad (8)$$

This means that at higher pressures the order with respect to hydrocarbon is zero and the experimental rate constant

$$r = k^0p_{H_2} \quad (9)$$

is identical with the true rate constant k_3. In the limit of lower pressures a first order results with an apparent rate constant $k_3K_1K_2$. Different degrees of approximation of zero order, as sometimes reported [ref. (*6*), p. 135] may explain deviations from the linear plot log k^0 versus π-complex stability.

It must be proved that the present model is consistent with the procedure of Smith and Campbell in determining the coefficients of adsorption. Their calculation is based on the Langmuir isotherm. Equation (7) represents such an isotherm, too, related to the equilibrium

$$A_g + s_\sigma = A_\sigma \quad (10)$$

with an overall coefficient of adsorption, split into two terms, the coefficient of adsorption from gas to A_π and the constant of the A_π–A_σ transition. According to this model the relative coefficients of adsorption, determined by Smith and Campbell, are then related to

$$A_l + s_\sigma = A_\sigma \quad (11)$$

The assumption of two kinds of adsorption obviously means that the directly measured amount of adsorption depends on both coefficients of adsorption. The opposed sequence of the coefficients shows that the measured adsorption is mainly of the π-type. So the number of occupied A_σ sites in vapor-phase measurement is low compared with the number of π-bonded molecules.

A further remark is necessary. In the procedure of Smith and Campbell it is essentially that in the pure phase reaction is $\sigma = 1$, which means that the experimental rate constant is the true one [compare Eq. (9)]. In the above model different sites for both adsorbed species are postulated to fulfill this requirement. With respect to this, competitive adsorption of A_π and A_σ on identical sites must be abandoned.

π–σ Mechanism of Hydrogenation

The surface π-complex (Fig. 6, I) is considered as a necessary precursor of the reactive σ-state. The π-bonding is strengthened by the increasing number of methyl groups, but the bonding in the A_σ state should be weakened by the methyl groups according to the opposite trend of the relative coefficients of adsorption. We propose a σ-bonded species (Fig. 6, II) which has a tilted position, whereas the π-bonded one lies flat on the surface. The third and slow step is the attack of hydrogen at the carbon atom neighboring to the metal-bonded one forming a species identical to that resulting in a dissociative adsorption of a saturated hydrocarbon, as assumed in dehydrogenation (*17*) (Fig. 6, III). The further hydrogenation goes quickly.

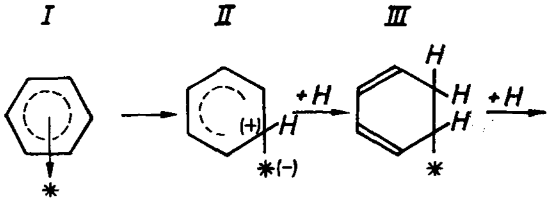

FIG. 6. Proposed π–σ mechanism of hydrogenation of aromatic hydrocarbons.

It should be emphasized that the proposed mechanism is in accordance with the usual role of π- and σ-complexes as intermediates in reaction mechanisms of unsaturated hydrocarbons, in which the π-complexes are conceived as low-energy intermediates that precede the formation of high-energy σ-complex intermediates (*18*).

The mechanism presented differs from the dissociative mechanism in hydrogen exchange, as proposed by Garnett *et al.* (*4*), only in considering the σ-state as a stable one and not as a transition state. In Rooney's (*3*) mechanism there are only π-bonded species assumed. Horrex, Moyes, and Squire (*19*) find that both these mechanisms will explain their results in toluene hydrogenation. Recently similar π-complex mechanisms are proposed in homogeneous catalysis, too, in hydrogenation by Lipovich *et al.* (*20*), and in hydrogen exchange by Garnett *et al.* (*21*).

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