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The Kinetics, Stereochemistry, and Mechanism of Hydrogenation of Some Tertbutylbenzenes on a Rhodium Catalyst[1]

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The kinetics and stereochemistry of the rhodium-on-alumina-catalyzed hydrogenation of 1,3- (**1**) and 1,4-di-t-butylbenzene (**2**) have been examined to seek clarification of the mechanism of hydrogenation of the benzene ring. The influence of structure upon the rate is illustrated through comparisons with the rate of hydrogenation of t-butylbenzene (**11**) and 4-t-butyltoluene (**12**). Near atmospheric pressure, the rates are zero order in arene, first order in hydrogen, and increase in the sequence **11**, **1** < **12** < **2**. In competitive experiments, the order of reactivity is **11** > **12** > **1** > **2** which yields the relative adsorption coefficients of 3×10^2, 45, 3, and 1, respectively. The possibility that a dissociatively adsorbed benzene is an important entity in the mechanism is discounted because **2** does not exhibit an unusual kinetic order in hydrogen. At low pressures (0.3–2 atm) about 80% of the initial products from **2** is 1,4-di-t-butyl-cyclohexene (**3**), the remainder being *cis*-1,4-di-t-butylcyclohexane (**6**). The latter may have formed from the hydrogenation of *cis*-3,6-di-t-butylcyclohexene (**5**) which is also observed. In the low pressure range, the maximum concentration of the intermediate increases with pressure presumably because the rate of hydrogenation of **3** is less dependent upon the hydrogen pressure than the hydrogenation of **2**. The 1,4-ene, **3**, is isomerized to **5** which adds hydrogen faster than does **3**. At high hydrogen pressures, the direct conversion of **2** to saturated products is the dominant process and most of the intermediate **3** is hydrogenated without prior isomerization. Much smaller amounts of the intermediate cyclohexenes are formed from **1** although increasing the pressure increases the maximum amount which is observed (1% at 1 atm, 3.5% at 30 atm). At high pressures (>30 atm) both **1** and **2** yield small amounts of the intermediates. Apparently the orientation of the bulky t-butyl substituents in the arene not only affect the rate of hydrogenation but also determine the proportion of products which are formed via the subsequent alternative reaction paths.

INTRODUCTION

The kinetics of hydrogenation of benzene and some of its alkyl derivatives on group VIII metals have been reported in a number of papers; however, the available information allows for a variety of mechanistic interpretations (*1–5*). The use of isotopes (*6*) or stereochemistry (*7*) has aided in the selection of the more from the less probable mechanisms, but the situation is unsettled (*8*). In this paper we report experiments, using a rhodium on alumina catalyst, with benzenes substituted by t-butyl groups which, through their bulk, alter the rates or completely block some of the kinds of reactions which occur during the catalytic hydrogenation of benzene (*9*). The bulky substituents also affect the relative rates of reduction of the arene and the derived cyclohexene(s) so that unusually large amounts of the

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[1] (a) Presented in part before the First North American Meeting of the Catalysis Society, Atlantic City, N.J., February 20, 1969. (b) Taken in part from the M.S. (1969) and the Ph.D. Thesis of James Outlaw, Jr., University of Arkansas (1971).

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latter are observed often (*10*). Our results bear upon the nature and role of some of the intermediates which are formed in the course of saturating the aromatic ring.

Initially, we sought to compare the kinetics of hydrogenation of 1,3-(**1**) and 1,4-di-t-butylbenzene (**2**) to distinguish between one of the more frequently postulated mechanisms (*5*) and one which appeared to us to have greater virtue. To illustrate the argument we begin with the classical Horiuti and Polanyi mechanism for the addition of hydrogen which can be represented by the elementary reactions

$$H_2 + * \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2H(ads) \quad (1)$$

$$C_6H_6 + * \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} C_6H_6(ads) \quad (2)$$

$$C_6H_6(ads) + H(ads) \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} C_6H_7(ads) \quad (3)$$

$$C_6C_7(ads) + H(ads) \xrightarrow{k_4(\text{slow})} C_6H_8(ads) \xrightarrow{\text{fast}} C_6H_{12}, \quad (4)$$

where the asterisk (*) represents a surface site (*11, 12*). Madden and Kemball showed that the kinetics of the reaction on nickel, first order in hydrogen and zero order in benzene, are consistent with this mechanism if the rate-limiting step is reaction (4), the combination of C_6H_7(ads) with another adsorbed hydrogen atom, the remaining steps being fast and essentially irreversible under the usual reaction condition (*5*). Similar kinetics for benzene hydrogenation often are observed when other group VIII metals are used as catalysts (*2*).

One might have guessed that reaction (3) would be the slow step because the aromaticity of the benzene structure is destroyed upon the addition of the first hydrogen atom. Indeed kinetic expressions identical to those obtained by Kemball and others can be derived from this assumption if one also assumes that a sizeable fraction of the active sites are covered by species of the composition C_6H_5(ads) formed reversibly from benzene (Eq. (5)) (*13*).[2]

$$C_6H_6 + * \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} C_6H_5(ads) + H(ads). \quad (5)$$

Farkas and Farkas suggested long ago that this latter reaction accounts for the catalytic exchange of benzene with deuterium (*14*). In concluding their review of the chemisorption of benzene on metal surfaces, Moyes and Wells suggested that serious consideration be given to the possibility that the formation of a σ-adsorbed phenyl (C_6H_5(ads)) precedes the formation of a π-adsorbed benzene (C_6H_6(ads)) (*8*).

To test these ideas we decided to compare the kinetics of hydrogenation of **1** and **2**. The former, like benzene, is capable of dissociative adsorption, the latter is not, as judged by the failure of t-butylbenzene to undergo exchange with deuterium at positions *ortho* to the tertiary butyl group (*9*). If reaction (4) is rate limiting and if no more than a small fraction of the sites at which the hydrogenation of an arene can occur holds dissociatively adsorbed arene (reaction (5)), then both compounds should exhibit the usually observed kinetics, first order in hydrogen. However, if these sites are mainly occupied by dissociatively adsorbed arene when allowed by the arene structure, the common situation, then to account for the rate being first order in hydrogen, one would conclude that reaction (3) is rate limiting. Accordingly, if the hydrogenation of **2** has the same rate-limiting step, then its rate of hydrogenation should be one-half order in hydrogen because **2** cannot form the dissociated intermediate.

Although these considerations directed our attention to this study, the unusually

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[2] The derivation is based upon the assumption of Langmuir–Hinshelwood kinetics and the relationship between the fraction of sites occupied by various molecular species and the concentrations of reactants to which they are related as proposed in (*13*).

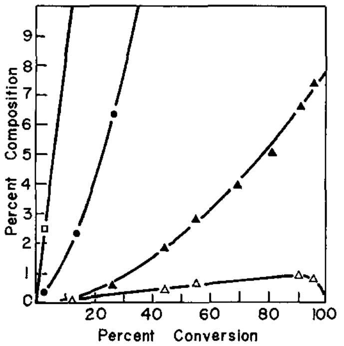
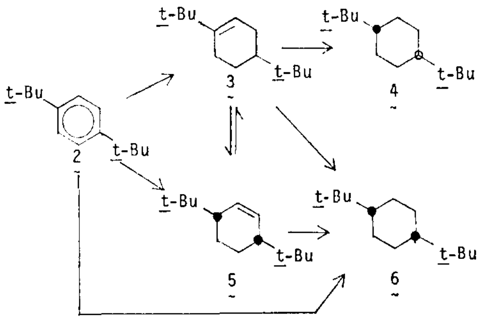


FIG. 1. Product distribution versus percentage conversion of 1,4-di-t-butylbenzene (2) (5% rhodium on alumina, 30°C, 0.84 atm); 1,4-di-t-butylcyclohexene (□), 3,6-di-t-butylcyclohexene (△), *cis*-1,4-di-t-butylcyclohexane (●), and *trans*-1,4-di-t-butylcyclohexane (▲).

large amount of cycloalkene formed, particularly from **2**, permitted a detailed study of the behavior of this intermediate under the conditions used in hydrogenating arenes, and therefore, the influence of the pressure of hydrogen upon the transformations of 1,4-di-t-butylcyclohexene (**3**) was examined also.

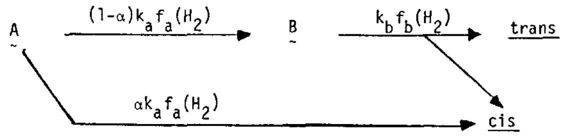
RESULTS

Formation and reactions of intermediates from 1,4-di-t-butylbenzene. In accordance with expectation based upon the work of van Bekkum and his associates (*9*), the hydrogenation of 1,4-di-t-butylbenzene (**2**) yields 1,4-di-t-butylcyclohexene (**3**) as the principal initial product (~80%), the remainder being mainly *cis*-1,4-di-t-butyl cyclohexane (**6**). *trans*-1,4-Di-t-butylcyclohexane (**4**) is not an initial product but is formed by the subsequent reduction of 1,4-di-t-butylcyclohexene. *cis*-3,6-Di-t-butylcyclohexene (**5**) is also produced; its concentration rises steadily and reaches a value of about 1% of the initial concentration of the arene (see Fig. 1).



During the course of the hydrogenation of arene **2**, the relative rate at which the intermediate 1,4-ene is formed and disappears is a function of the pressure of hydrogen (Fig. 2) (*15*). Curiously, the maximum concentration of the intermediate which is observed *increases* with *increasing* pressure as the hydrogen pressure is raised from 0.3 to 1.0 atm, but the maximum *decreases* with *increasing* pressure as the pressure is raised above about 3 atm. Clearly, this results from the difference in the manner by which the pressure of hydrogen affects the rate of addition of hydrogen to the arene and to the intermediate alkene, respectively.

In terms of the principal molecular species observed, a kinetic scheme which reproduces the observed phenomena can be derived as follows:



A fraction (α) of the 1,4-di-t-butylbenzene (**A**) which is reduced is assumed to be converted directly to *cis*-1,4-di-t-butylcyclohexane while the remainder, ($1-\alpha$), first forms 1,4-di-t-butylcyclohexene (**B**), the amount of *cis*-3,6-di-t-butylcyclohexene being neglected for simplicity. Both the *trans* and the *cis* saturated isomers are formed by the reduction of **B**. The rate of the hydrogenation of the arene is a function of the hydrogen pressure, $f_a(H_2)$, while the rate of hydrogenation of the intermediate is a different function of the pressure of hydrogen, $f_b(H_2)$. Assuming Langmuir–Hinshelwood kinetics, the rate of hydrogenation of **A** and the formation and disappearance of **B** are given by Eqs. (6) and (7) where $[\mathbf{A}]_{ads}$ represents the fraction of reactive surface sites which hold **A** and K_A and K_B are the equilibrium constants for adsorption of **A** and **B**, respectively. The relative change in concentrations of **A** and **B** is given by Eq. (8) which on integration gives Eq. (9) where N_B is the mole fraction of **B** present at N_A, the mole fraction of **A** which has been converted to products *(16)*.[3]

$$\frac{-d[\mathbf{A}]}{dt} = k_a[\mathbf{A}]_{ads} f_a(H_2) = \frac{k_a K_A[\mathbf{A}] f_a(H_2)}{1 + K_A[\mathbf{A}] + K_B[\mathbf{B}]} \tag{6}$$

$$\frac{d[\mathbf{B}]}{dt} = \frac{(1-\alpha)k_a K_A[\mathbf{A}] f_a(H_2) - k_b K_B[\mathbf{B}] f_b(H_2)}{1 + K_A[\mathbf{A}] + K_B[\mathbf{B}]} \tag{7}$$

$$\frac{d[\mathbf{B}]}{d[\mathbf{A}]} = \frac{(1-\alpha)k_a K_A[\mathbf{A}] f_a(H_2) - k_b K_B[\mathbf{B}] f_b(H_2)}{k_a K_A[\mathbf{A}] f_a(H_2)} \tag{8}$$

$$N_B = \frac{S(1-\alpha)}{S-1}\left[(1-N_A)^{1/S} - (1-N_A)\right] \tag{9}$$

where

$$S = \frac{k_a K_A f_a(H_2)}{k_b K_B f_b(H_2)}$$

The parameters α and S which furnish the fit to the data, as shown in Fig. 2, are tabulated in Table 1. Clearly both parameters are functions of the pressure of hydrogen. The value of α is greater at the higher pressure which indicates that the fraction of arene, which is transformed to saturated products without forming the intermediate 1,4-di-t-butylcyclohexene, is greater at high than at low hydrogen pressures. The variation of S with increasing pressure shows that the rates of hydrogenation of the arene and the intermediate are different functions of the hydrogen pressure.

Apparently, in the low pressure range, an increase in the hydrogen pressure, though increasing the rate of the hydrogenation of the arene **2** (see below), has a lesser effect upon the rate of hydrogenation of 1,4-di-t-butylcyclohexene (**3**). Under these conditions, the reduction of **3** is determined mainly by the rate at which it is isomerized to *cis*-3,6-di-t-butylcyclohexene (**5**) which itself is hydrogenated more rapidly than is **3**.

The transformations of 1,4-di-t-butylcyclohexene (**3**) are illustrated in Fig. 3 where the curves, representing the mole fraction of *cis*-3,6-di-t-butylcyclohexene **5** as a function of the conversion of **3**, are almost independent of pressure in the range of 0.3–6 atm. 1,4-Di-t-butylcyclohexene reverts in part to 1,4-di-t-butyl-

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[3] The same equation has been used to interpret the effect of intraparticle diffusion upon the selectivity for the formation of an intermediate in a reaction sequence A → B → C *(16)*. However, see *(31)*.

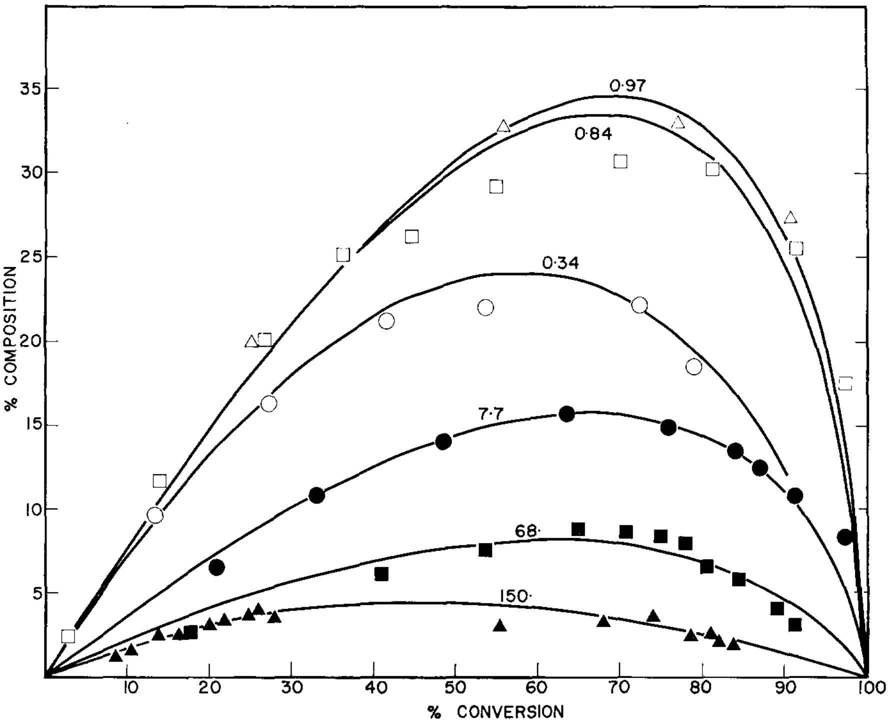


FIG. 2. The effect of the pressure of hydrogen (in atmospheres) upon the mole fraction of 1,4-di-t-butylcyclohexene formed as a function of the conversion of 1,4-di-t-butylbenzene. The curves are calculated from Eq. (9) using the parameters given in Table 1. Data are indicated by the symbols: ○, □, △, ●, ■, ▲ for the pressures 0.34, 0.84, 0.97, 7.7, 68, and 150 atm, respectively.

benzene (**2**), the proportion which does so decreasing with increasing pressure.

The cis and trans saturated products. Both 1,3- and 1,4-di-t-butylbenzene yield a greater fraction of the *cis* than of its *trans* saturated isomer at low conversions than at high as is expected if the *trans* isomer results from the reduction of a desorbed substituted cyclohexene. With increased pressure, the *cis* isomer constitutes a greater fraction of the first-formed saturated product from the 1,4-arene; at complete reduction, however, the relative amounts of *cis* and *trans* products are not greatly affected by the pressure (Table 2). As the pressure of hydrogen is raised, the smaller fraction of the intermediate cyclohexene (**3**) which is formed yields an increasingly larger proportion of the *trans* saturated product.

TABLE 1

The Kinetics of Formation of Intermediates in the Hydrogenation of 1,4-Di-t-Butylbenzene, Parameters for Eq. (9)

P_{H_2} (Atm)	α	S
0.34	0.24	0.65
0.84	0.20	1.30
0.97	0.20	1.40
7.7	0.61	1.20
68.0	0.77	0.90
150.0	0.80	0.40

The hydrogenation of the 1,3-arene **1**, yields a greater fraction of the *trans* saturated product at high pressures than at low pressure, as noted below. Increasing the pressure results in an increase in the maximum concentration of the intermediate cyclohexene.

Intermediates from 1,3-di-t-butylbenzene (**1**). A relatively small fraction of the

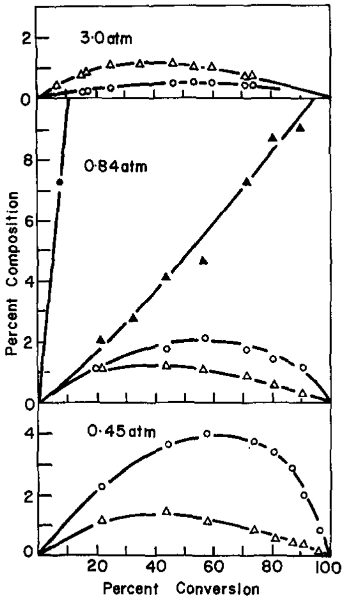


FIG. 3. The effect of hydrogen pressure upon the distribution of products obtained from 1,4-di-t-butylcyclohexene (5% rhodium on alumina, 30°C); *cis*-1,4-di-t-butylcyclohexane (●), *trans*-1,4-di-t-butylcyclohexane (▲), *cis*-3,6-di-t-butylcyclohexene (△), and 1,4-di-t-butylbenzene (○).

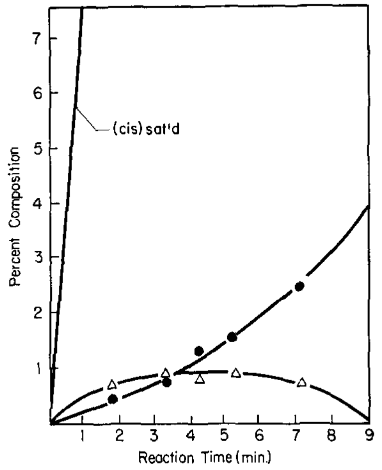


FIG. 4. Product distribution versus time for the hydrogenation of 1,3-di-t-butylbenzene (1) (5% rhodium on alumina, 30°C, 0.84 atm of hydrogen); total 1,3- and 2,4-di-t-butylcyclohexene (△), *trans*-1,3-di-t-butylcyclohexane (●).

initial product of the hydrogenation of 1,3-di-t-butylbenzene (**1**) appears as a mixture of 1,3- (**7**) and 2,4-di-t-butyl-cyclohexene (**8**), the principal product being *cis*-1,3-di-t-butylcyclohexane (**9**) (Fig. 4). When the pressure of hydrogen is increased, the proportion of the intermediates also increases to a maximum of about 3 to 4 mol% at about 40% conversion at 35 atm. The rate of hydrogenation of arene **1** also increases. Thus although the rate of conversion of 1,3-di-t-butylbenzene to these

TABLE 2

The Percentage of *trans* Product Formed as a Function of Pressure and Percentage Conversion (in Parenthesis)

Pressure (atm)	1,4-Arene (2)	1,4-ene (3)	1,3-Arene (1)
0.45	—	8.4 (44)	—
0.84	8.2 (20), 11.0 (100)	9.4 (44), 10.5 (100)	1.9 (20), 3.9 (100)
6.0	—	12.3 (45)	3.2 (18)[a]
7.7	5.0 (33), 9.3 (90)[a]	—	3.3 (22),[a] 5.2 (40)[a]
34.0	—	—	8.3 (20),[a] 8.5 (50)[a]
68.0	7.0 (20), 10.0 (37)	14.6 (40)	10.0 (23)
150.0	7.0 (20), 9.5 (84)	—	—

[a] Reference (*15*).

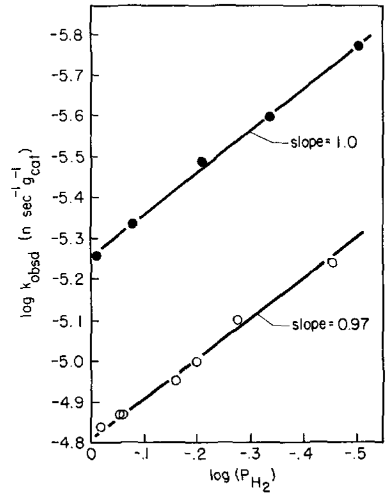


FIG. 5. Pressure dependence of the rate of hydrogenation of 1,4-di-t-butylbenzene (○), at 25°C, and 1,3-di-t-butylbenzene (●), at 30°C, catalyzed by 5% rhodium on alumina.

TABLE 3

The Competitive Hydrogenation of Substituted Aromatic Hydrocarbons over 5% Rhodium on Alumina

Hydrocarbon pairs		Equilibrium adsorption constants ($K_{i,k}$)[a]	Initial rate ratios ($k_k°/k_i°$)
i	*k*		
1,3-di-t-Bu (**1**)	1,4-di-t-Bu (**2**)	3.1	1.69
t-Bu (**11**)	1-Me-4-t-Bu (**12**)	10.0	1.38
1-Me-4-t-Bu (**12**)	1,4-di-t-Bu (**2**)	45.0	1.25
t-Bu (**11**)	1,4-di-t-Bu (**2**)	—[b]	1.75
t-Bu (**11**)	1,3-di-t-Bu (**1**)	50.0	1.03

[a] $K_{i,k} = \theta_i C_k/\theta_k C_i = b_i/b_k$ where $K_{i,k}$ is the equilibrium constant for adsorption between the compound *i* and *k*, and b_i, C_i, and $k_i°$ are the coefficients of adsorption, the concentration, and the initial rate constant, respectively, for hydrocarbon *i* (*17*).

[b] When 1,4-di-t-butylbenzene and t-butylbenzene are reduced competitively only 1.6% of 1,4-di-t-butylbenzene is consumed while 85% of the t-butylbenzene is transformed.

intermediates must have a greater dependence on the pressure of hydrogen in the low-pressure region than does the hydrogenation of the intermediates, this relationship extends to a higher pressure than is observed with 1,4-di-t-butylbenzene. At higher pressures (>60 atm) the 1,3-arene, **1**, produces about the same fraction of intermediate (**7** and **8**) as does the 1,4-arene (**2**) which indicates similarities in the mechanism and the relative reactivity of arene and intermediate cycloalkene(s) under high hydrogen pressures.

Kinetics of hydrogenation of the arenes. In the low-pressure range, the rate of hydrogenation of 1,4- or 1,3-di-t-butylbenzene, as well as the other arenes examined, is zero order in arene and first order in hydrogen, a result commonly found (Fig. 5). Elsewhere we have shown that at high pressure, the kinetics of hydrogenation of 1,4-di-t-butylbenzene (**2**) on the rhodium catalyst is anomalous (*15*). The kinetic anomaly apparently results from the effect of high hydrogen pressures upon the rhodium catalyst which reduces its activity. Arenes which are more strongly bound to the catalyst than is **2** seem to inhibit this change in activity. The 1,3 isomer (**1**) behaves normally in that increasing the pressure increases, in direct proportion, its rate of hydrogenation (*15*).

Competitive hydrogenations. Smith and Campbell (*17*) have reported that *para*-xylene is reduced faster than *meta*-xylene while the *meta* isomer is more strongly adsorbed than the *para* isomer. The same relationship holds for 1,3- (**1**) and 1,4-di-t-butylbenzene (**2**) (Table 3). However, the magnitude of the adsorption equilibrium constant ($K_{1,2} = 3.1$) and the ratio of the initial rate constants ($k_2°/k_1° = 1.69$) for the disubstituted t-butyl compounds are both larger than the respective parameters for the *para*- and *meta*-xylenes, $k_{m,p} = 1.9$, $k_p°/k_m° = 1.40$. The relative effects of a t-butyl and a methyl group on the strengths of adsorption of aromatic hydrocarbons is also seen in the competitive hydrogenation between 1,4-di-t-butylbenzene (**2**) and 4-t-butyltoluene (**12**) for which $k_{12,2} = 45$. The effect of a t-butyl group is even more pronounced in the competitive reduction of t-butylbenzene (**11**) and 1,4-di-t-butylbenzene. For in this instance 1,4-di-t-butylbenzene is almost completely excluded from the surface until all the t-butylbenzene has been reduced. When the 1,3 isomer is reduced competitively with t-bu-

TABLE 4

Rate Constants ($k_i°$) and Relative Adsorption Coefficients (b_i) for the Hydrogenation of Substituted Aromatic Hydrocarbons (5% Rh–Al_2O_3, 30°C)

Compounds (*i*)	Initial rate constants, 10^6 $k_i°$		Relative adsorption coefficients, b_i[b]
	Observed[a]	Relative	
1,4-di-t-Bu (**2**)	9.22	(1.0)	1
1,3-di-t-Bu (**1**)	5.46	0.59	3
1.Me-4-t-Bu (**12**)	7.37	0.80	45
t-Bu (**11**)	5.33	0.58	3×10^2

[a] The observed $k_i°$ values have the units mol sec^{-1} g^{-1} atm^{-1} for experiments performed at 30°C and 0.84 atm of hydrogen and with catalyst No. 13-434.

[b] Determined via the method of Smith and Campbell (*17*).

tylbenzene the relative adsorption equilibrium constant of 50.0 is obtained. However, the rate of reduction is comparable ($k_1^\circ/k_{11}^\circ = 1.03$) in contrast to $k_2^\circ/k_{11}^\circ = 1.74$ for the *para* isomer and t-butylbenzene. Similar effects of t-butyl substituents have been reported for hydrogenations catalyzed by Pt/C and Pd/C (*9c*).

From the results summarized in Table 4 it is clear that the adsorption of both 1,3- and 1,4-di-t-butylbenzene is considerably weaker than the adsorption of aromatic hydrocarbons substituted with less bulky groups. The origin of this effect probably is steric since electronic differences among alkyl groups would be expected to be relatively small (*18*).

DISCUSSION

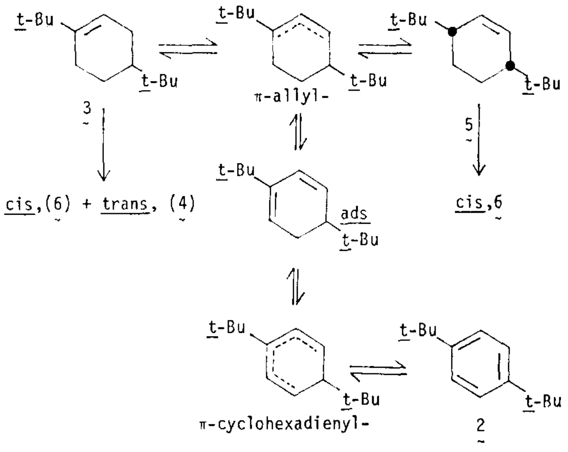
Kinetics. If the Langmuir–Hinshelwood model is correct the fact that the kinetics of hydrogenation of both 1,3- and 1,4-di-t-butylbenzene show a first-order dependence on the pressure of hydrogen indicates that reaction (4) is rate limiting. The results imply that the amount of dissociatively adsorbed aromatic hydrocarbon (σ-complex) which can be in equilibrium with the undissociated form must be small even for compounds such as benzene or 1,3-di-t-butylbenzene which are not prevented by steric factors from forming the σ-complex. Otherwise the 1,4 isomer (2) would have exhibited a rate which is proportional to the one-half power of the pressure of hydrogen. Accordingly we must conclude, as did Madden and Kemball (*5*), that the transition state of the rate-controlling step consists of the catalyst site, the aromatic hydrocarbon, and two atoms of hydrogen.

As to subsequent steps, the present results show that at moderate pressures of hydrogen the majority, if not all of 1,4-di-t-butylbenzene which becomes saturated, forms an intermediate cyclohexene which is desorbed from the catalyst. The principal intermediate is 1,4-di-t-butylcyclohexene (**3**); however, another intermediate may be *cis*-3,6-di-t-butylcyclohexene (**5**) whose rapid conversion to *cis*-1,4-di-t-butylcyclohexane would obscure the path by which the latter is formed.

In the low-pressure range, the hydrogenation of the 1,4-ene (**3**) is in part direct and in part indirect via isomerization to the 3,6-ene (**5**) which is hydrogenated more rapidly. Relative to their rates of addition, the interconversion of **3** and **5** must be fast because as **3** is transformed to products the relative concentrations of **5** and **3** rapidly approach a ratio which is almost independent of pressure from 0.3 to 3.0 atm (see Fig. 3).

The fraction of the 1,4-ene (**3**) which is hydrogenated directly rather than via **5** can be estimated from the *cis* to *trans* ratio of saturated products formed and the assumption that **5** yields only *cis*-1,4-di-t-butylcyclohexane while the addition of hydrogen to **3** gives more of the *trans* than the *cis* isomer as is expected for the addition of hydrogen to a 4-t-butyl-substituted cyclohexene (*19*). If one assumes that **3** yields about 65% of the *trans* isomer as does 4-t-butyl-1-methylcyclohexene at 1 atm on reduced platinum oxide, a reaction which appears to occur without appreciable isomerization of the alkene, then about 13% of **3** is reduced directly at 0.45 atm and 16% at 0.84 atm. If instead, one assumes that **3** would yield equal amounts of *cis* and *trans* isomers, the fractions of direct reduction become 0.17 and 0.20, respectively. Accordingly in this pressure range, over 80% of the 1,4-di-t-butylcyclohexene (**3**) which is converted to saturated products does so via isomerization to *cis*-3,6-di-t-butylcyclohexene (**5**).

The isomerization of **3** to **5** is likely to proceed via the formation of a π-allylic intermediate (*20*) which would also lead to the formation of arene **2** as observed in the scheme below (*21*).



It is of interest to note that the relative rate of formation of the arene from **3** is inversely proportional to the pressure of hydrogen (Fig. 3). This relationship is required in order to be consistent with the observed kinetics of the reverse reaction. Thus, the rate of formation of arene **2** from **3** is determined by the rate of the transfer of one hydrogen atom from an absorbed dienic intermediate whose surface concentration is proportional to the concentration of **3** and inversely proportional to the pressure of hydrogen.

At high pressures, the mechanism of hydrogenation of 1,4-di-t-butylbenzene is altered. It appears improbable that an increase in pressure should increase appreciably the proportion of *cis*-3,6-di-t-butylcyclohexene which might be formed initially from 1,4-di-t-butylbenzene. Accordingly, we conclude that at high pressure, most of the arene is converted to the saturated product without desorption of any unsaturated intermediate. The saturated isomer formed in this way should be the *cis*, however, the ratio of *cis* to *trans* isomers formed at high pressure is lower than that formed at low pressures of hydrogen. Therefore, the smaller fraction of the intermediate alkene formed at high pressure must yield a larger fraction of the *trans* saturated product upon the addition of hydrogen than it does when it is reduced at low pressures. Indeed, 1,4-di-t-butylcyclohexene does yield a greater portion of *trans*-1,4-di-t-butylcyclohexane at high than at low pressures. The result is in accordance with expectation for the stereochemistry of the direct addition of hydrogen to the 1,4-ene (*19*).

Generally, increasing the hydrogen pressure diminishes the importance of alkene isomerization via an allylic intermediate. For example, using a platinum on alumina catalyst, Weitkamp (*22*) showed that at high pressures, the addition of deuterium to 1,9-octalin and its isomerization to 9,10-octalin occurs through a common alkyl intermediate whereas, Smith and Burwell (*20*) had concluded that at low hydrogen pressures the isomerization of 9,10-octalin to 1,9-octalin and the addition of hydrogen to 9,10-octalin proceeded by different paths. The isomerization was thought to occur via an allylic intermediate.

At high pressures, the intermediate 1,4-ene is hydrogenated more rapidly than the precursor arene **2**. Thus the change from low to high pressures of hydrogen, which corresponds to a change from a hydrogen-deficient to a hydrogen-rich catalyst, has altered greatly the relative reactivity of arene **2** and the intermediate 1,4-ene. The change in relative reactivity may reflect the difference in the rate at which molecular hydrogen attacks adsorbed arene or alkene, respectively, relative to the rate at which arene or alkene react with adsorbed hydrogen.

Unlike **2**, 1,3-di-t-butylbenzene (**1**) yields a relatively small amount of the observable unsaturated intermediates, 1,3- and 2,4-di-t-butylcyclohexene. Although not determined experimentally, their rates of hydrogenation would be expected to be comparable to the rate of hydrogenation of the 1,4-ene and like the latter, the hydrogenations are likely to proceed in part via isomerization to an alkene which is not substituted at the double bond. If this is so, then one must conclude that either most of the 1,3-arene is hydrogenated directly to *cis*-1,3-di-t-butylcyclohexane without the desorption of any intermediate from the catalyst, or the principal cycloalkene intermediate which is formed at low pressures, although not detected, is *cis*-3,5-di-t-butylcyclohexene which would be converted rapidly to *cis*-1,3-di-t-butylcyclohexane. We hope to resolve this question by an appropriate experiment.

Conclusions. The mechanism of hydrogenation of these t-butylbenzenes on rhodium appears to be a multistep process in which the intermediate steps are readily reversed. Accordingly, the kinetics should be well described in terms of the Langmuir–Hinshelwood formalism and the conclusion that dissociatively adsorbed benzene has little significance in the kinetic scheme should be valid.

Although it is clear that at high hydrogen pressures, a large portion of 1,4-di-t-butylbenzene is converted to *cis*-1,4-di-t-butylcyclohexane without the desorption from the surface of any intermediate, whether the direct path is of any significance at low pressure is uncertain. Apparently, the products of each of the elementary steps, in which hydrogen is transferred to the adsorbed arene or to the adsorbed intermediate, are adsorbed species with the possible exception of the product of the elementary step in which the saturated product is formed (*21*). Whether unsaturated intermediates are observed depends upon the relative rates of the competing desorption of and hydrogen additions to the adsorbed dienes and monoenes (*23*). Alkyl substituents reduce the attraction between arene or alkene and the catalyst, and the steric effect of a t-butyl group must act in the same direction (*9*). Thus the ready observation of substituted cyclohexene intermediates when t-butyl substituted arenes are hydrogenated on rhodium catalysts is understandable. However, the strikingly different amounts of the intermediates observed from 1,3- and 1,4-di-t-butylbenzene seem to depend upon a factor other than the effect of substitution upon the relative reactivity of these arenes and the possible derived substituted cyclohexenes. The placement of the substituents in the arene may determine the orientation of the addition of hydrogen to the adsorbed arene and the subsequent hydrogen transfer which determine the proportion of the various possible adsorbed cyclohexenes which are formed. Recently, Niewstad *et al.* (*24*) have concluded from a detailed kinetic and stereochemical study of the hydrogenation of alkyl-substituted naphthalenes that the first hydrogen atom which is transferred to the adsorbed naphthalene adds preferentially so as to release steric strain in the adsorbed species. However, as noted before, the addition of the second hydrogen atoms occurs at the rate-controlling step, and this leads to an adsorbed diene. Presumably, the final distribution of products is determined by the structure of the diene which is formed in the rate-controlling step. We have attempted to explore this possibility through studies of the hydrogenation of the various dienes which are derived from 1,3- and 1,4-di-t-butylbenzene, and the result will be reported elsewhere.

EXPERIMENTAL

The NMR spectra were recorded on a Varian A-60 spectrometer with tetramethylsilane as the internal standard. Chemical shifts are reported in τ units, and the letter in the parenthesis designates the multiplicity of the signal: s, singlet; t, triplet; m, unresolved multiplet. Infrared spectra were obtained on a Perkin–Elmer Model 337 grating spectrophotometer. All preparative glc was done using a 15-ft × $\frac{1}{4}$-in.-o.d. column packed with 2% Carbowax 20 M on 45/60-mesh Chromosorb G in an Aerograph A90-P3 gas chromatograph equipped with a thermal conductivity detector. A hydrogen flame chromatograph was used with a 20-ft or 25-ft × $\frac{1}{8}$-in.-o.d. column packed with 2% polyethylene glycol 1000 distearate on Chromosorb W for quantitative glc measurements except for the analysis of the *cis*- and *trans*-1,4-di-t-butylcyclohexanes (**3** and **4**) in which a capillary column (300 ft × 0.02 in.) coated with purified Apiezon L was used (*25*).

1,3-Di-t-butylbenzene (**1**) was prepared from 3,5-di-t-butylphenol according to the procedure of Pines *et al.* (*26*) which begins with 2,4-di-t-butylphenol; and the intermediate 3,5-di-t-butylcyclohexene was aromatized directly. Final purification of **1** was achieved by preparative glc. At an oven temperature of 100°C and a carrier gas flow rate of 60 ml/min, *m*-di-t-butylbenzene (purity, 99%) eluted in 39 min.

The infrared and ultraviolet spectrum agreed well with that reported in the literature (*26*). NMR (CCl_4) τ 8.69 (s, 18, t-butyl groups), τ 2.85 (m, 3, ring hydrogens), τ 2.59 (m, 1, ring hydrogen).

1,4-Di-t-butylbenzene (**2**) (Eastman Grade, Eastman Organic Chemicals) was used as received (~99% pure by glc, mp 77–79°C).

t-Butylbenzene (**11**) and *t-butyltoluene* (**12**) were both research grade (99.95%, Phillips Petroleum Co.) and were used without further purification.

Solvent purification. To remove possible catalyst poisons from material used as a solvent in kinetic experiments, cyclohexane (200 ml, 99.5%, Phillips Petroleum Co.) was refluxed several hours over W–6 Raney nickel (10 g). Part (<1%) of the cyclohexane was converted to benzene, and after the mixture was distilled from the Raney nickel, the trace amount of benzene was hydrogenated to cyclohexane using 5% rhodium on alumina at 30°C and 1 atm of hydrogen. The cyclohexane was then redistilled after removal of the catalyst by filtration. The cyclohexane was shown to be free of benzene by glc analysis.

1,4-Di-t-butylcyclohexene (**3**) was prepared according to the procedure of Stolow and Ward (*27*). The NMR spectra of this material and samples collected via preparative glc from a partially reduced (5% rhodium on alumina, 30°C, 1.0 atm hydrogen) sample of 1,4-di-t-butylbenzene were identical with those previously reported. The preparation of *cis*-3,6-di-t-butylcyclohexene (**5**) will be given elsewhere.

cis- and trans-1,3-Di-t-butylcyclohexane (**9** and **10**) were distinguished for the purpose of glc analysis by equilibrating (250°C, 120 hr) a sample of completely reduced 1,3-di-t-butylbenzene (5% rhodium on alumina, 30°C, 0.84 atm hydrogen) over 5% palladium on carbon. The relative amounts of the *cis* and the *trans* isomers in the resulting mixture were virtually identical to the literature values (*28*).

Catalyst treatment. Typically, a batch (1.5 g) of 5% rhodium on alumina (Engelhard Industries, lot No. 3652 and 13-434) was heated (140 ± 4°C, 12–15 hr) and cooled in a stream of hydrogen. Before exposing the catalyst to air the heating chamber was flushed with nitrogen. Treatment above 150°C diminished the catalytic activity as determined by the rate of reduction of t-butylbenzene which served as a standard. The catalyst from lot No. 13-434 was one-half as active as that from lot No. 2652.

Hydrogenation apparatus and procedures. The kinetic experiments were performed at constant pressure (0.3–1.3 atm) in a semimicro apparatus consisting of a shaken reaction vessel connected to an automatic recording gas buret (*29*). The reactor assembly is similar to one described by Hussey (*30*). The lower section of the neck of the reaction flask was shaped so as to direct the solution reaching this region back to the center of the flask. The reaction flask was shaken by a Vortex Jr. Mixer. The vortical motion of the reaction solution caused by the mixer was broken up by a vertical crease in the lower half of the flask. The jacketed flask was maintained at a constant temperature by water circulated from a thermostated bath.

In a typical kinetic experiment prereduced catalyst (100 mg) was transferred quantitatively to a clean, dry reaction flask. After rigidly clamping the reaction flask in position on the mixer and connecting it to the vacuum line the entire system was evacuated and filled with hydrogen three times in order to eliminate air. To avoid catalyst poisoning by mercury vapors in the filling process, the hydrogen flow was directed away from the reactor toward the mercury sources. After the desired reaction pressure was set, purified cyclohexane (4–4.5 ml), was injected into the reaction flask, by way of the serum cap using a syringe. Subsequently the system was equilibrated by vigorous mixing for 10 to 15 min. Reactants were then injected into the reaction flask. In all experiments the initial adsorption of hydrogen occurred almost simultaneously with mixing.

The kinetic experiments were done at a constant rate of shaking and the initial rates of reduction were shown to be directly proportional to the weight of the catalyst. This demonstrates that the rate of transfer of hydrogen from gas to catalyst particle is not rate limiting (*31*).[4] To obtain samples of the reaction solution, the shaker was stopped, the catalyst allowed to settle, and then a small sample (approximately 0.05 ml) was withdrawn with an airtight syringe whose long needle was inserted through the syringe cap. When the shaker was restarted, the absorption of hydrogen proceeded at the rate observed before the interruption.

Competitive reductions for several pairs of aromatic hydrocarbons were performed and the results were analyzed in the manner described by Smith and Campbell (*17*).

Experiments performed at pressures between 1.3 and 6 atm were conducted in a 90-ml glass aerosol tube (Fisher and Porter Co.) (*32*). For pressures above 6 atm, a 300-ml stainless-steel high-pressure autoclave (Autoclave Engineers Inc., Model ABP-300) was used. By using a glass liner, the contact of the reactants with the stainless steel was limited to the internal cooling coil and the impeller which was driven at 400 rpm (*15*).

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[4] This does not assure that intraparticle diffusion does not affect the kinetics; however, the order of an intrinsic first-order reaction would not be affected while a lower or higher intrinsic order would move one-half an order toward first (*31*).

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