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The Catalytic Exchange and Deuteration of *tert*-Butylbenzene and *p-tert*-Butyltoluene on Evaporated Metal Films

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The catalytic exchange with deuterium and the deuteration of *tert*-butylbenzene have been investigated on films of palladium, tungsten, platinum, nickel, and sintered nickel using a mass spectrometer. The hydrogen atoms in the molecule can be divided according to their ease of exchange into groups of 3, 9, and 2 which are thought to be the ring atoms in the *meta* and *para* positions, the atoms on the side group, and finally the two ring atoms in the *ortho* positions. The bulky side group shows a pronounced steric deactivation on the reactivity of these last two atoms but its influence on the exchange of the other ring atoms or on deuteration is not nearly so great. The hydrogen atoms in the side group are replaced at rates which are comparable to those found for the exchange of neopentane and which are much lower than the rates of exchange of hydrogen atoms on the β carbon atoms of molecules like ethylbenzene and cumene.

Some observations on the exchange and deuteration of *p-tert*-butyltoluene on films of nickel and tungsten were also made.

The results of this investigation are discussed with emphasis on the differences between the mechanism of the heterogeneous metal-catalyzed exchange and the homogeneous acid-catalyzed exchange reactions of the alkylbenzenes. However, the same reaction path may not operate for ring exchange on all metals and there is some evidence which suggests that tungsten may differ from the other metals and may, possibly, involve a dissociative mechanism.

INTRODUCTION

Studies of the exchange of a series of alkylbenzenes with deuterium on evaporated films of nickel (*1*) have shown that the hydrogen atoms in the molecules can be classified into groups according to their relative ease of exchange. The most reactive were those on carbon atoms α to the benzene ring or in ring positions not *ortho* to a side group, next in order of reactivity came those atoms *ortho* to one side group, followed by those on β and γ carbon atoms in compounds with side groups larger than methyl, and finally by those in ring positions *ortho* to two side groups. On sintered (*1*) or poisoned (*2*) films, the rates of exchange of all groups were reduced but the rates of ring exchange were decreased more than those of side-group exchange.

The cause of the lowered activity at positions in the ring *ortho* to a side group has not been established clearly. Crawford and Kemball (*1*) were inclined to discount the influence of steric hindrance because there was no apparent correlation between the size of the side group and the rate of exchange in the *ortho* position. Furthermore, Garnett and Sollich (*3*) had shown that in the platinum-catalyzed exchange of the halogeno-benzenes with heavy water the reactivity of the *ortho* hydrogen atoms which were the least reactive of the ring atoms increased with increasing size of the halogen substituent. We thought that it would be worthwhile examining the exchange of *tert*-

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butylbenzene to see to what extent the presence of a really large substituent would affect the rate of exchange of any or all of the ring hydrogen atoms. There was a further reason for choosing this compound. We wanted to see whether the reactivity of the hydrogen atoms on the β carbon atoms in *tert*-butylbenzene, which has a quaternary carbon atom in the α position, differed from the reactivity of the corresponding hydrogen atoms in ethylbenzene or cumene.

Some work on the exchange of *tert*-butyl benzene with heavy water has been reported recently by Garnett and Sollich (*4*). They found that the ring hydrogen atoms in the *meta* and *para* positions were replaced over active platinum at a rate which was some 170 times slower than the rate of exchange of benzene under similar conditions. They found no exchange of the two *ortho* hydrogen atoms and no data were obtained about side-group exchange. As the rate and character of catalytic exchange reactions of the alkylbenzenes often differ substantially when heavy water is used instead of deuterium, we did not modify our proposed investigation.

EXPERIMENTAL

The apparatus and the general technique were similar to those described previously (*1*, *5*)—reactions were carried out in a glass vessel linked by a capillary leak to a Metropolitan-Vickers MS2 mass spectrometer.

Reagent grade *tert*-butylbenzene (British Drug Houses, Ltd.) was purified by heating under reflux at atmospheric pressure for 15 hr with approximately 10% by weight of Raney nickel catalyst, the water under which the latter was stored having been removed by azeotropic distillation. The treated material was distilled and examined for purity by gas-liquid chromatography and infrared spectral analysis. There was about 3% of an unidentified impurity, probably an isomer, which did not appear to interfere with the reactions. Material which had not been treated with the Raney nickel catalyst did not exchange with deuterium on nickel films below about 250°C. A similar treatment was used to purify *p-tert*-butyltoluene of purissimo grade obtained from the Aldrich Chemical Co. The only impurity detected was a small amount of the *meta* isomer. Both compounds were dried with activated molecular sieves (Linde 5A) and further purified by distillation under vacuum and then by outgassing before each experiment.

Typical reaction mixtures consisted of either 0.62 mm of *tert*-butylbenzene or 0.28 mm of *p-tert*-butyltoluene and a 20:1 ratio of deuterium:hydrocarbon. The numbers of aromatic molecules in the reaction vessel (198 ml) were 4.3×10^{18} or 2.0×10^{18}, respectively.

For the mass spectrometric analyses, an ionizing beam of 25 V was used and parent ions in the range of masses from 134 to 148 (*tert*-butylbenzene) or 148 to 164 (*p-tert*-butyltoluene) were measured to determine the isotopic content of the molecules. With both compounds the amount of fragmentation involving the loss of hydrogen or deuterium atoms was negligible and so the only corrections made to the observed peak heights were those for the naturally occurring heavy carbon and deuterium. When deuteration occurred to form the corresponding substituted cyclohexanes, estimates of the rate were obtained by the decrease in the peaks due to the parent aromatic ions. This method had to be used as the amounts of the parent cyclohexane ions in the mass spectrometer were too low for accurate analysis. The decrease in the height of the peaks due to the parent aromatic ions was corrected for losses other than by deuteration by reference to experiments in which the same quantities of reactants were brought in contact with films which were either poisoned or unreactive at the temperatures being examined.

When sintered films of nickel were required, they were prepared by evaporating the metal onto the walls of the reaction vessel maintained at 200°C.

RESULTS

Examination of the distributions of products with time during the exchange of *tert*-butylbenzene on palladium films or on films of sintered nickel showed that the hydrogen atoms in the molecule could be divided according to their rate of exchange into three groups, A, B, and C, consisting of 3, 9, and 2 atoms, respectively. Group B must correspond to the atoms in the side chain, Group A was believed to contain the ring atoms in the *meta* and *para* positions, and *Group* C the two ring atoms in the *ortho* positions. With films of tungsten, platinum, and nickel, three atoms, obviously Group A, were always replaced rapidly but the full extent of the next group of hydrogen atoms to be exchanged could not be determined before the aromatic molecule was removed by deuteration to form *tert*-butylcyclohexane. We believe that the second group to exchange on these metals was Group B, by analogy with the results on palladium and sintered nickel, but we cannot rule out the possibility of some slight contribution from exchange of Group C.

$$-\log_{10}(\phi_\infty - \phi) = k_\phi t/2.303\phi_\infty - \log_{10}\phi_\infty \qquad (1)$$

where k_ϕ is the initial rate of entry of deuterium atoms into 100 molecules of reactant in unit time and ϕ is defined by

$$\phi = \Sigma i d_i \qquad (2)$$

d_i representing the percentage of the isotopic species containing i deuterium atoms at time t; ϕ_∞ is the equilibrium value of ϕ. The initial rate of disappearance of the d_0 hydrocarbon in percentage in unit time, k_0, may also be obtained from the equation

$$-\log_{10}[d_0 - (d_0)_\infty] = k_0 t/230.3 - \log_{10}[100 - (d_0)_\infty] \qquad (3)$$

where $(d_0)_\infty$ is the equilibrium value of the percentage of the light hydrocarbon. The mean number of deuterium atoms replaced initially in each molecule undergoing exchange is given by the ratio

$$M = k_\phi/k_0 \qquad (4)$$

With *tert*-butylbenzene, containing hydrogen atoms which react at different rates, the quantities k_ϕ and k_0 will be composite terms of the type

$$k_\phi = k_A + k_B + k_C \qquad (5)$$

and

$$k_0 = k_{0A} + k_{0B} + k_{0C} \qquad (6)$$

and plots according to Eq. (1) will not be linear. Approximate methods may be used

TABLE 1

SOME DISTRIBUTIONS OF ISOTOPIC *tert*-BUTYLBENZENES DURING EXCHANGE

Catalyst	Temp. (°C)	ϕ^a	d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8	d_9	d_{10}	d_{11}	d_{12}	d_{13}	d_{14}
Pd	50	123	23.5	39.7	26.9	9.9	—	—	—	—	—	—	—	—	—	—	—
Pd	100	840	—	—	—	—	—	2.9	8.3	15.1	23.7	25.7	18.4	5.5	0.4	—	—
Pd	150	1128	—	—	—	—	—	—	—	—	1.0	4.6	13.8	36.1	36.8	6.2	1.5
W	25	298	—	0.9	3.7	92.6	2.5	0.3	—	—	—	—	—	—	—	—	—
Pt	50	332	—	0.6	2.2	70.2	19.5	6.7	0.8	—	—	—	—	—	—	—	—
Ni	50	295	0.2	1.4	7.0	86.3	5.1	—	—	—	—	—	—	—	—	—	—
Sintered Ni	175	257	6.8	17.2	24.7	27.9	14.0	6.5	1.8	0.9	0.2						
Sintered Ni	225	1056	—	—	—	—	—	—	1.1	3.5	5.9	10.8	19.6	29.1	25.7	4.1	0.2

[a] The value of ϕ indicates the extent of the exchange reaction; the mean number of deuterium atoms in the molecules is $\phi/100$.

Some typical distributions of products at different stages of the exchange reactions are shown in Table 1; several of these show a definite break in the distributions between the d_3 and the d_4 compound and others show that d_{13} compound is substantially lower than the d_{12} compound.

Methods of Analyzing the Kinetic Data

The methods used to determine the rates of exchange of the different groups of hydrogen atoms were similar to those described previously (*1*, *6*).

When all the hydrogen atoms in a molecule react at the same rate, the course of the exchange reaction is given by the equation to determine the rates of exchange of the groups of hydrogen atoms and work satisfactorily provided that $k_A > k_B > k_C$.

In order to determine k_C and k_{0C}, we assumed that the d_{12} compound had exchanged the Group A and the Group B hydrogen atoms and that the formation of the d_{13} and d_{14} compounds was due to the exchange of the two hydrogen atoms in Group C. Thus, we defined quantities ϕ_C and x_C by the relations

$$\phi_C = 100(d_{13} + 2d_{14})/(d_{12} + d_{13} + d_{14}) \quad (7)$$

and

$$x_C = 100d_{12}/(d_{12} + d_{13} + d_{14}) \quad (8)$$

and these were used in place of ϕ and d_0, respectively, in equations similar to Eq. (1) and Eq. (3). Care was required in selecting the values to be used for $\phi_{C\infty}$ and $x_{C\infty}$. If we had been able to measure the total concentration of deuterium in the two positions corresponding to Group C it would have been correct to determine $\phi_{C\infty}$ by the relationship

$$\phi_{C\infty} = (2/14)\phi_\infty \quad (9)$$

However, we were only able to measure the exchange in the Group C positions in molecules which had already exchanged all their Group A and Group B hydrogen atoms and so a smaller value of $\phi_{C\infty}$ was appropriate. The method used was to calculate an equilibrium distribution corresponding to $\phi_\infty = 1240$ for the exchange of all 14 hydrogen atoms in the molecule, assuming a random distribution of the 12.4 deuterium atoms between the various isotopic species. Values of $(d_{12})_\infty$, $(d_{13})_\infty$, and $(d_{14})_\infty$ of 27.7%, 33.0%, and 18.3% were obtained in this manner and hence by Eq. (7) and Eq. (8) we found $\phi_{C\infty} = 88$ and $x_{C\infty} = 35.0$, respectively. Satisfactory plots according to the modified form of Eq. (1) were obtained with this value of $\phi_{C\infty}$, as shown in Fig. 1, whereas use of the higher value of $\phi_{C\infty} = 177$ based on Eq. (9) gave curved lines.

The exchange of the Group B hydrogen atoms was investigated by assuming that the d_3 compound had exchanged the Group A hydrogen atoms and that the formation of the higher compounds was a consequence of the exchange of the Group B and Group C hydrogen atoms. Thus, we defined ϕ_B by the equation

$$\phi_B = 100\left[\sum_4^{12} (i - 3)d_i + 9(d_{13} + d_{14})\right] \Big/ \sum_3^{14} d_i \quad (10)$$

and used this in an equation similar to Eq. (1). The rate determined in this manner was $k_B + k_C$ and in cases where we had no knowledge of the value of k_C we assumed that it could be neglected in comparison with k_B. The sum $k_{0B} + k_{0C}$ was found in a similar way by using x_B, defined as

$$x_B = 100d_3 \Big/ \sum_3^{14} d_i \quad (11)$$

in place of d_0 in Eq. (3); again, where k_{0C} was not known it was neglected.

By analogy with the procedures just described, we found that it was preferable to determine k_ϕ by using ϕ_A, defined as

$$\phi_A = d_1 + 2d_2 + 3\sum_3^{14} d_i \quad (12)$$

in a modified version of Eq. (1) which gave a good linear plot rather than by using Eq. (1) directly. Values of k_A were then found from Eq. (5). Typical plots using ϕ_A and ϕ_B in the appropriate versions of Eq. (1) are shown in Fig. 1, and the good straight lines obtained provide some support for the methods chosen to interpret the kinetic data.

The mean numbers of deuterium atoms replaced initially in each group of atoms were obtained from the relationships

$$M_A = k_A/k_{0A} \qquad M_B = k_B/k_{0B} \quad \text{and} \quad M_C = k_C/k_{0C} \quad (13)$$

tert-Butylbenzene

If we were able to determine the rates of exchange of any of the groups of hydrogen atoms or the rates of deuteration on a given catalyst over a range of temperatures, the results are summarized by the appropriate Arrhenius parameters which are given in Table 2. Rates of reaction which could not be studied over a range of temperatures are either quoted in the text or shown in Table 3,

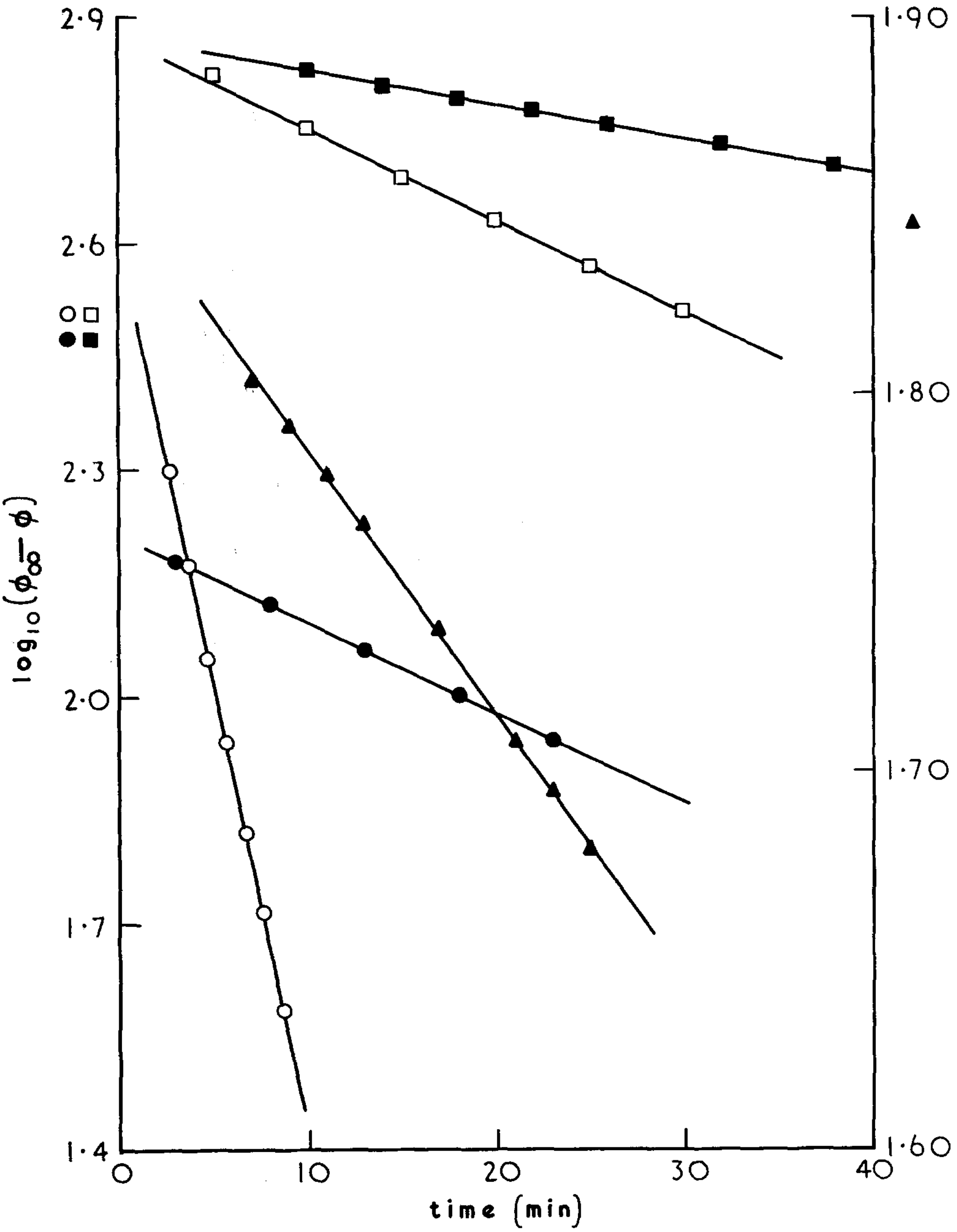

FIG. 1. Plots based on equations similar to Eq. (1) for the exchange of the different groups of hydrogen atoms in *tert*-butylbenzene. Group A, with ϕ_A defined by Eq. (12): ○, on 13.7 mg tungsten at 0°C; ●, on 18.9 mg sintered nickel at 125°C. Group B, with ϕ_B defined by Eq. (10): □, on 14.9 mg palladium at 100°C; ■, on 18.9 mg sintered nickel at 150°C. Group C, with ϕ_C defined by Eq. (7) and $\phi_{C\infty} = 88$: ▲, on 13.0 mg sintered nickel at 250°C.

which compares rates for the different catalysts and reactions at 0°C.

Palladium. Exchange of the Group A and Group B atoms was investigated in the temperature range 25° to 100°C. The Group C atoms were only replaced at a measurable

TABLE 2
ARRHENIUS PARAMETERS FOR THE EXCHANGE AND DEUTERATION OF *tert*-BUTYLBENZENE

Catalyst	Reaction	Temp. range (°C)	E (kcal/mole)	$\log_{10} A$ (A in mol./sec 10 mg)	Temp. for $k = 1\%$/min 10 mg (°C)	M
Pd	*m*-, *p*-Ring exchange	25 to 75	16.8 ± 0.6	26.6 ± 0.6	38	1.0_6 to 1.3_9
Pd	Side-group exchange	75 to 100	25.0 ± 1.5	30.3 ± 1.0	81	1.0_5 to 1.7_6
W	Deuteration	0 to 25	11.4 ± 1.3	23.4 ± 1.6	20	—
Pt	Side-group exchange	25 to 50	20.1 ± 1.0	29.1 ± 1.0	36	1.1 to 1.2
Pt	Deuteration	0 to 50	10 ± 2	22 ± 2	(22)	—
Ni	Side-group exchange	25 to 70	17.5 ± 1.4	25.9 ± 0.5	82	1.0 to 1.9
Ni	Deuteration	0 to 75	8.5 ± 0.3	20.3 ± 0.3	67	—
Sintered Ni	*m*-, *p*-Ring exchange	99 to 150	22.3 ± 1.7	27.2 ± 1.9	123	1.2 to 1.3
Sintered Ni	Side-group exchange	125 to 175	25.1 ± 2.3	27.8 ± 1.9	151	1.2 to 1.3
Sintered Ni	*o*-Ring exchange	200 to 250	30.1 ± 2.8	27.4 ± 2.5	252	1.0 to 1.2

TABLE 3
RATES OF REACTIONS OF *tert*-BUTYLBENZENE AT 0°C

	Rates (%/min 10 mg)				
	Pd	W	Pt	Ni	Sintered Ni
Group A exchange	2.2×10^{-2}	44	11	83	3×10^{-6}
Group B exchange	3×10^{-5}	(1.5×10^{-2})[a]	1.4×10^{-2}	1.3×10^{-3}	7×10^{-8}
Group C exchange	(5×10^{-9})[b]	—	—	—	3×10^{-12}
Deuteration	(10^{-3})[c]	2.3×10^{-1}	2×10^{-1}	4.6×10^{-2}	—

[a] Based on 0.15%/min 10 mg at 25°C and an assumed value of 15 kcal/mole for E.
[b] Based on 0.18%/min 10 mg at 125°C and an assumed value of 30 kcal/mole for E.
[c] Assuming 1%/min 10 mg at 150°C and 10 kcal/mole for E.

rate at 125°C or above; a typical value of k_{0C} at 150°C was 0.25%/min 10 mg with $M_C = 1.4$. Deuteration was slow at 150°C but a reliable rate could not be obtained.

Tungsten. The rate for Group A exchange, which occurred rapidly at 0°C with $M_A = 1.5$ is given in Table 3; Group B exchange was slow at 25°, the rate being 0.15%/min 10 mg with $M_B = 1.1$. Above 25° deuteration was so rapid that exchange rates could not be measured.

The portion of the mass spectrum corresponding to the parent ions of the saturated product, *tert*-butylcyclohexane, was not sufficiently intense to be studied but an analysis was made of the peaks corresponding to the loss of a methyl group from this compound. The composition of these ions at the stage when deuteration was just completed indicated that this reaction involved principally the addition of six atoms and that not more than 0.3 hydrogen atom was exchanged during deuteration. The *tert*-butylcyclohexane, once formed, did not appear to undergo further exchange at 25°C but gained more deuterium at higher temperatures.

Platinum. There was a general similarity between the results on platinum and those on tungsten. Group A hydrogen atoms exchanged rapidly at 0°C with $M_A = 1.1$, and the exchange of Group B occurred at 25°C. No rates of exchange could be obtained above 50°C because deuteration was too fast; the distribution shown in Table 1 was measured when 80% of the *tert*-butylbenzene had been deuterated.

The investigation of the extent of the exchange which accompanied deuteration was difficult with platinum because the exchange of the Group B atoms and deuteration proceeded at comparable rates at 50°C. There was also overlap between the ions from the cyclohexanes involving the loss of a methyl group and the *tert*-butylbenzene parent ions; the cyclohexanes produced were found to exchange slowly at this temperature. Within the limits of the experimental error, it seemed that deuteration occurred mainly by a simple addition of atoms without accompanying exchange.

Nickel. A very rapid exchange of the Group A hydrogen atoms took place at 0°C with $M_A = 2.2$. Group B atoms were observed to exchange very slowly at 25°C but even at higher temperatures the range of isotopic species formed was never extensive due to the removal of the aromatic molecule by deuteration.

Sintered nickel. No exchange at a measurable rate occurred below 100°C and the difference between the reactivities of the Group A and the Group B hydrogen atoms was much less marked than on the nickel films laid down at 0°C. Arrhenius parameters for the exchange of all three groups of atoms are given in Table 2.

Above 125°C, the peak heights of the ions from the aromatic molecule decreased slowly with time but no ions were detected to indicate the formation of the substituted cyclohexane. The rate of disappearance of *tert*-butylbenzene rose to about 1%/min 10 mg at 250°C and scans over the whole mass spectrum indicated that the molecule was undergoing some type of hydrogenolysis at these high temperatures.

p-tert-Butyltoluene

A few observations were made on the exchange of *p-tert*-butyltoluene in order to provide data for comparison with results for toluene (*1*) and with the results for *tert*-butylbenzene. Quantitative work was limited because of the low vapor pressure.

Tungsten. Deuteration was fast at 0°C and so accurate rates of reaction could not be obtained. However, rough values of about 20%/min 10 mg were found for both exchange and deuteration. Five hydrogen atoms were replaced, three being exchanged somewhat more rapidly than the remaining two.

Nickel. Three hydrogen atoms were exchanged at 0°C with $k_0 = 3.7\%$/min 10 mg and $M = 1.65$ and at 25°C, the respective figures were 15.0 and 1.98. The values of k_0 correspond to an activation energy of about 10 kcal/mole.

A slow exchange of two further hydrogen atoms was just observable at 25°C and the rate at 100°C was 0.33%/min 10 mg with $M = 1.28$. A further group began to exchange at this temperature and products up to d_{14} were observed at 150°C. Deuteration at 100°C was not faster than 0.2%/min 10 mg.

DISCUSSION

It is obvious that the large *tert*-butyl group has a striking effect in reducing the rate of exchange of the *ortho* hydrogen atoms in *tert*-butylbenzene on palladium. The exchange of benzene with deuterium occurs at 0.14%/min 10 mg on palladium at 0°C (*7*) and so even allowing for substantial error in the extrapolated rate for the Group C exchange given in Table 3, the decrease in rate due to the large substituent is a factor of over 10^7. The corresponding reduction in rate for ring exchange of *p*-xylene on palladium (*6*) is only 130 and so the *tert*-butyl group has a much greater deactivating effect on the exchange at the *ortho* position than a methyl group. Our results in this respect agree well with those of Garnett and Sollich (*4*) for the exchange with heavy water over a platinum catalyst at 120°C because they reported a "complete" deactivation at the *ortho* position of *tert*-butylbenzene. The primary influence of the large substituent must be steric.

The rates of exchange of the *meta* and *para* ring positions in *tert*-butylbenzene are only about an order of magnitude slower than the corresponding rates of exchange of benzene on platinum and palladium (*7*), the rates being lower by factors of 20 and 6, respectively, on the two metals. Thus, the effect of the *tert*-butyl substituent on these positions in the ring is not so marked as in the reactions with heavy water, where at factor of 170 was found (*4*). A comparison of the rate for Group A exchange on nickel, given in Table 3, with the rates of exchange of the *meta*- and *para*-hydrogen atoms in toluene, ethylbenzene, cumene, and *n*-propylbenzene (*1*) shows that all rates are similar and hence that the effect of the *tert*-butyl group on the reactivity of these positions is about the same as that of the smaller alkyl groups.

The results for the exchange of *tert*-butylbenzene on the metals show many differences from the behavior of the same molecule when it is subjected to homogeneous acid-catalyzed exchange (*8*). In acid solutions, the exchange is believed to involve electrophilic substitution by a conventional associative mechanism (*9*) and there is little steric hindrance to the replacement of hydrogen atoms in the *ortho* positions even with side groups as large as the *tert*-butyl group. In contrast, steric effects are marked with exchange on the metal catalysts and the normal directing effects associated with electrophilic substitutions are not observed. Furthermore, the enhanced rates which are commonly found with alkyl substitution in the benzene ring in the homogeneous exchange are not apparent in the heterogeneous reactions. Garnett and Sollich (*4*) pointed out that the large steric effect of the *tert*-butyl group on the reactivity at the *ortho* positions and the smaller influence on other ring positions, as observed in the heterogeneous exchange with heavy water, are compatible with the formulation of ring exchange by a dissociative mechanism. They argued against an associative mechanism on the grounds that this should not be subject to steric effects because the associative mechanism in homogeneous acid-catalyzed exchange is not sterically hindered. We believe that this type of argument is not valid and that it may be misleading to assume that concepts relevant to the acid-catalyzed exchange of the alkylbenzenes are directly applicable to the metal-catalyzed heterogeneous systems. It is possible that either the nature of the adsorbed aromatic molecule is significantly different from such a molecule in solution or, perhaps more likely, the deuterium which enters the molecule is essentially neutral and not an ionic species. It follows that if an associative mechanism occurs with the metals it will involve the addition of a chemisorbed atom to the adsorbed aromatic molecule (or the addition of one of the two atoms in a molecule of deuterium, the second becoming chemisorbed) and we should expect steric effects to be important, especially for exchange in the *ortho* position near a bulky group.

We believe that the steric effects which we have observed and those found by Garnett and Sollich (4) with *tert*-butylbenzene do not unambiguously favor a dissociative as opposed to an associative mechanism of ring exchange. Aside from this difficult problem, one would expect the bulky side group to interfere with the adsorption of the molecule in a form involving bonding between the π orbitals and a metal atom and with the aromatic ring parallel to the surface. It is possible that some limited association of part only of the π system with the surface atoms occurs and it is perhaps relevant to note the recent evidence (*10*) that a benzene ring can be coordinated simultaneously to two palladium atoms, each of which is bonded to three carbon atoms of the ring. If such an interaction permitted a bent structure for the benzene ring so that it behaved as two allylic systems, an adsorption involving the *meta* and *para* positions only might be of importance with *tert*-butylbenzene.

The rate of exchange of the *tert*-butyl group on nickel films is markedly reduced in comparison with the rates of exchange of the hydrogen atoms attached to the β carbon atoms of ethylbenzene, *n*-propylbenzene, or cumene (*1*). These last three compounds all show such exchange at about the same rate and this is some 2000 times faster than the exchange of the Group B atoms in *tert*-butylbenzene. It is interesting to compare the rate of exchange of the *tert*-butyl group with the rate of exchange of neopentane (*11*) on the various metals, as may be seen from the results in Table 4. The rates of the two reactions are similar on nickel and also on tungsten but the aromatic molecule exchanges faster than neopentane on palladium. Thus, with the possible exception of catalysis on palladium, the presence of the quaternary carbon atom prevents any substantial influence of the phenyl group on the reactivities of the hydrogen atoms in the methyl groups of *tert*-butylbenzene. The hydrogen atoms in methyl groups attached to quaternary carbon atoms are not readily exchanged on metal catalysts as shown by the present work, the results with neopentane (*11*), and by earlier investigations as well (*12*, *13*).

TABLE 4
COMPARISON OF THE RATES OF EXCHANGE OF THE *tert*-BUTYL GROUP IN *tert*- BUTYLBENZENE AND OF NEOPENTANE

Catalyst	*tert*-Butyl group Temp. (°C)	Rate (%/min 10 mg)	Neopentane[a] Temp. (°C)	Rate (%/min 10 mg)
Pd	100	5.0	112	5.5×10^{-2}
W	25	1.5×10^{-1}	25	7.1×10^{-1}
Ni	50	1.8×10^{-1}	55	9.0×10^{-2}

[a] Taken from ref. (*11*).

TABLE 5
APPROXIMATE RATIOS OF THE RATES OF RING EXCHANGE TO DEUTERATION FOR *tert*-BUTYLBENZENE AND BENZENE ON DIFFERENT METALS AT 0°C

Compound	Pd	W	Pt	Ni
tert-Butylbenzene	(~20)[b]	200	~60	1800
Benzene[a]	7.4	~0.3	30	>1000

[a] Taken from ref. (*7*) and (*14*).

[b] Based on assumptions given under Table 3.

Some data on the relative rates of ring exchange and deuteration for benzene and for *tert*-butylbenzene are given in Table 5. Although the results are only approximate, three of the metals, palladium, platinum, and nickel, show roughly similar ratios of the rates for both compounds. Thus, on these three metals the effect of the bulky substituent seems to be much the same on both the exchange and the deuteration of the aromatic compound. In contrast, the ratio of the rates of the two reactions is much larger on tungsten for *tert*-butylbenzene than for benzene and so on this metal the presence of the bulky group has a less severe effect on exchange (in the *meta* and *para* positions) than it has on deuteration. It is tempting to suggest that ring exchange might involve an associative mechanism on palladium, platinum, and nickel in order to account for the common influence of the side group on exchange and deuteration (which must involve associate steps) and that the diverse effects on tungsten are due to a dissociative mechanism of the exchange process. While these suggestions may be barely justifiable, it is important at any rate to bear in mind the possibility that different mechanisms of ring exchange may operate on different metals.

The results in Table 3 show that the rates of the exchange reactions are very much slower on sintered nickel films than on films laid down at 0°C. This fact is obvious although it would be wrong to place too much reliance on the actual rates quoted for sintered films. Firstly, these are obtained by extrapolations over considerable ranges of temperature and, secondly, another factor may influence the comparison between the two types of films. As temperatures of above 100°C are needed to give measurable rates of exchange on the sintered films, there is at least a possibility that the surfaces are partially blocked by hydrocarbon radicals formed by dissociation involving rupture of the carbon–carbon bonds of the reactant. Such breakdown is much more likely to be important at the temperatures used for catalysis on the sintered films than at the lower temperatures at which the ordinary nickel films were studied. Thus the rate of reaction on sintered films may be reduced and the activation energy raised by the presence of these species and both these factors will tend to exaggerate the differences between the rates of exchange on the two kinds of films at 0°C. Nevertheless, it is clear that the effect of sintering is much more marked on the rate of exchange in the *meta* and *para* positions in the ring than on the rate of exchange of the side group, the factors being 10^7 and 10^4, respectively. This means that the change in the relative rates of the two kinds of exchange is in general accord with the earlier observations on other compounds (*1*); special sites which are destroyed by sintering may be necessary for ring exchange.

The ratio of the rates of exchange of the *meta* and *para* hydrogen atoms to the rate of exchange of the *ortho* hydrogen atoms on sintered nickel films is about 10^6 at 0°C and this is almost identical to the corresponding ratio on palladium.

A number of points merit comment in the results for *p-tert*-butyltoluene. The grouping of the hydrogen atoms in this molecule is clearly 3, 2, 9, 2 and the most easily exchanged are those on the methyl group followed by the two *ortho* to this group. The exchange of the methyl group on nickel at 0°C is about 15 times slower than the exchange of the methyl group of toluene (*1*) at this temperature and so the presence of the bulky *tert*-butyl group in the *para* position does not interfere greatly with exchange of the methyl side group. However, there is a greater influence of the bulky group on the reactivity of the two hydrogen atoms *ortho* to the methyl group. In toluene these exchange quite readily at −10°C but at 25°C or even at 100°C the rate is small with *p-tert*-butyltoluene. In other words, if we bring the results for Group A exchange of *tert*-butylbenzene on nickel into the comparison, we can say that the combined deactivation of a methyl group *ortho* to a ring position and a *tert*-butyl group *meta* to the same position is much more substantial than the influence of either group alone. It is not easy to see why the bulky group in the *meta* position should have such an influence if a dissociative mechanism of ring exchange operates on nickel. In contrast, on tungsten the exchange of the two hydrogen atoms *ortho* to the methyl group in *p-tert*-butyltoluene occurs fairly readily at 0°C and the rate, despite the presence of the methyl group, is only a factor of about 10 lower than the rate of Group A exchange for *tert*-butylbenzene. So on tungsten, there is a much less marked combined deactivation of ring exchange due to a methyl group in the *ortho* position and the *tert*-butyl group in the *meta* position and this may be interpreted as evidence in favor of a dissociative mechanism of ring exchange.

There are some remarkable differences in the rates of deuteration of *tert*-butylbenzene and *p-tert*-butyltoluene on tungsten and nickel which we cannot explain. Whereas the deuteration of *p-tert*-butyltoluene is about 100 times faster on tungsten than the deuteration of *tert*-butylbenzene, the corresponding ratio on nickel is about 10^{-2}.

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