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The Hydrogen Exchange Reaction Between Benzene and Perdeuteriobenzene Catalyzed by Evaporated Metal Films

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The hydrogen exchange reaction between benzene and perdeuteriobenzene at 0°C has been investigated using evaporated films of molybdenum, rhodium, palladium, silver, tantalum, tungsten, rhenium, iridium, and platinum.

The reaction occurs readily over all of these metals, but over platinum and palladium the expected equilibrium is not attained. This is interpreted in terms of poisoning of the catalyst with strongly adsorbed material. There is no reaction over gold.

The rate constants for the reaction show a linear relationship with the percentage *d* character of the metallic bonds. The reaction is thought to occur through the formation of dissociatively adsorbed species on the metal surface in those cases where reaction occurs readily. Associatively adsorbed species may account for the anomalous features of the reaction on palladium and on platinum.

INTRODUCTION

Two mechanisms for the metal-catalyzed substitution of deuterium for hydrogen in aromatic compounds have been proposed. Crawford and Kemball (*1*) have favored an associative mechanism in order to interpret the exchange of alkylbenzenes. Garnett and Sollich-Baumgartner (*2*) investigated the reaction of a number of aromatic hydrocarbons with deuterium oxide and suggested a mechanism which involves the formation of a species by dissociation at the catalyst surface. The latter authors point out the importance of the randomization reaction in differentiating between these two mechanisms, having found the rate of this reaction to be almost the same as the rate of exchange between benzene and deuterium oxide using the same catalyst. Fraser and Renaud (*3*) examined the relative rates of the platinum-catalyzed exchange of deuterium oxide with the ortho, meta, and parahydrogen atoms in monosubstituted benzenes and concluded that the mechanism involved dissociative adsorption. They criticized Garnett's experiments, suggesting that, at the pressures used by Garnett, hydrogen was likely to be left on the catalyst surface before the reactants were admitted. Hirota *et al.* (*4*) investigated the self-exchange reaction in monodeuteriotoluenes catalyzed by nickel and by platinum, which they also interpret in terms of the dissociative mechanism.

Tetenyi (*5, 6*) has reported experiments in which ^{14}C-labelled benzene was chemisorbed on nickel. Some of this material could be desorbed by addition of further benzene at 150°C, but some required hydrogen treatment at 300°C. This evidence led these workers to suggest that dissociative chemisorption of benzene occurs on nickel. Erkelens and Burck (*7*) have obtained infrared spectra of benzene chemisorbed on silica-supported nickel and copper. They interpret their results in terms of the loss of aromatic character rather than the formation of a π-complex as with organometallic complexes.

Parravano (*8*) has examined the reaction between ^{14}C-labelled benzene and saturated cyclic C_6 hydrocarbons. He concludes that, for five alumina-supported metals at 117°C, benzene is π-adsorbed only on iridium.

We have investigated the reaction between benzene and perdeuteriobenzene on evaporated metal films because a variety of hydrogen-free metal catalysts in this form can be prepared in high vacuum rather than by reduction of a metal salt. A further reason for choosing this system was that a comparison could be made with results obtained for other reactions on metal films, particularly of reactions between aromatic hydrocarbons and deuterium, rather than deuterium oxide. As earlier workers have investigated a limited number of metals, it was also important to find out whether the reaction occurred over a wider range of catalysts. This provides an opportunity for studying the effect of the metal on the reaction, by comparing metal activities.

EXPERIMENTAL

Apparatus. The main features of the apparatus have been described (*9*). It consisted of a gas-handling system linked to a single focussing mass spectrometer. Frequent analyses of the reaction mixture was possible through a slow leak between the reaction vessel and the mass spectrometer. Three reaction vessels of volumes 880, 390, and 250 cm^3 were used so that percentage rates could be determined readily over a wide range of catalyst activity.

Materials. Analar grade benzene (C_6H_6) and Puriss grade perdeuteriobenzene (C_6D_6) (Koch-Light Laboratories Ltd.) were used. Corrections were made for the small amount of C_6HD_5 in C_6D_6. The hydrocarbons were mixed in equal molar proportions by weight, and the composition and purity were checked by mass spectrometry. They were degassed before use by repeated freezing, pumping, and thawing.

Metal wires of high purity were obtained from Johnson Matthey Ltd., Engelhard Industries Ltd., and Koch-Light Laboratories Ltd.

Technique. The technique used was similar to that published by Kemball (*10*). The glass walls of the reaction vessel were degassed by heating to 450°C for about 3 hr. The metal wires were heated electrically to just below evaporation temperature during the final hour of this treatment. The pressure just before evaporation was $\sim 10^{-4}$ N m^{-2} (10^{-6} mm Hg) measured on an ionization gauge close to the reaction vessel and the period of treatment depended on the time taken to reach this pressure.

Some films were prepared using a metal ultrahigh-vacuum system with a glass reaction vessel. In this apparatus, films could be deposited at pressures down to $\sim 10^{-7}$ N m^{-2} (10^{-9} mm Hg).

The reaction vessel was cooled at 0°C, and the metal evaporated on to the walls of the vessel by increasing the current through the wire. Wires of the metal required were used alone, or, in the case of platinum, palladium, gold, and silver supported on a suitable refractory metal wire. The mixture of benzene and perdeuteriobenzene was admitted to fill a mixing bulb at such a pressure that, on expansion into the reaction vessel, the final pressure was 66 N m^{-2} (0.5 mm Hg) of each reactant. Mass spectrometric analyses were carried out with an ionizing beam of 10-V electrons; under this condition no significant material at mass 77 was observed. The usual corrections were made for ^{13}C.

RESULTS

The reaction should go to an equilibrium state in which the deuterium and hydrogen are randomly distributed throughout the seven possible benzenes C_6H_6 to C_6D_6. This equilibrium was observed on rhodium and iridium. The agreement between the values calculated and those found using a rhodium catalyst is shown in Table 1.

In order to obtain rate constants which may be compared with those reported for the exchange of benzene with deuterium, a form of equation similar to that used by Anderson and Kemball (*11*) was devised. The rate equation is

$$\ln(\phi_\infty - \phi_F) = (k_F t/\phi_\infty) - \ln \phi_\infty, \quad (1)$$

where $\phi_F = \Sigma i d_i$, and d_i is the percentage isotopic species containing i deuterium atoms at time t, where i takes the values 1, 2, and 3. The rate of reaction was obtained from the relative amounts of C_6H_5D.

TABLE 1
COMPARISON OF CALCULATED AND EXPERIMENTAL EQUILIBRIUM PERCENTAGES OF BENZENES, EQUILIBRATED ON A RHODIUM FILM

	Calculated	Found
C_6H_6	1.6	1.8
C_6H_5D	9.4	9.8
$C_6H_4D_2$	23.4	23.3
$C_6H_3D_3$	31.2	31.2
$C_6H_2D_4$	23.4	23.3
C_6HD_5	9.4	9.0
C_6D_6	1.6	1.6

$C_6H_4D_2$, and $C_6H_3D_3$. Because $C_6H_3D_3$ could arise equally from the addition of deuterium to benzene or from the removal of deuterium from perdeuteriobenzene, the contribution of $C_6H_3D_3$ to the value of ϕ_F was halved. Equally the reverse reaction can be investigated where $\phi_R = \Sigma i d_i$, and in which d_i is the percentage of isotopic species containing i hydrogen atoms, and i takes the values 1, 2, and 3. In this case

$$-\ln(\phi_\infty - \phi_R) = (k_R t/\phi_\infty) - \ln(\phi_\infty - \phi_0), \qquad (2)$$

where ϕ_0 is the initial value of ϕ.

k_F and k_R are the constants for the initial rate of entry of deuterium or hydrogen atoms into 100 molecules of hydrocarbon/min/mg-cat. at the beginning of the reaction and ϕ_∞ is the equilibrium value of ϕ_F and ϕ_R.

The initial rate of disappearance of the reactants can also be found from the mass spectral measurements. These rates are described by the empirical equations

$$-\ln(d_0 - d_{0_\infty}) = k_0 t/(100 - d_{0_\infty}) - \ln(100 - d_{0_\infty}), \qquad (3)$$

and

$$-\ln(d_6 - d_{6_\infty}) = k_6 t/(100 - d_{6_\infty}) - \ln(100 - d_{6_\infty}), \qquad (4)$$

where d_0 and d_6 are the percentages of C_6H_6 and C_6D_6 respectively, and d_{0_∞} and d_{6_∞} are the equilibrium values of d_0 and d_6. These equations are similar to those used by Garnett and Sollich-Baumgartner (*2*).

This analysis generates four rate constants obtained from the slopes of the appropriate graphs: k_F for the addition of deuterium to benzene; k_0 for the disappearance of benzene; k_R for the addition of hydrogen to perdeuteriobenzene, and k_6 for the disappearance of perdeuteriobenzene.

The units of these rate constants are percentage min^{-1} $(\text{mg-cat.})^{-1}$. Reaction rates in vessels of different volume were compared by converting these constants to the units percentage of μmole min^{-1} $(\text{mg-cat.})^{-1}$. This is permissible because the same pressures of reactants were used, and so will not affect the surface coverage. Typical plots of $\ln(\phi_\infty - \phi_F)$ and of $\ln(d_0 - d_{0_\infty})$ versus time are shown in Fig. 1.

The ratios of the rate constants for incorporation of isotope to the rate constant for loss of reactant, M, represent the mean number of hydrogen or deuterium atoms replaced in each molecule undergoing exchange in the initial stages of the reaction (*9*). In this case the value can be found twice;

$$M_F = k_{F/k_0}; \text{ and } M_R = k_{R/k_6}.$$

The value of quoting k_0, k_6, k_F, and k_R when k_0 and k_F appear sufficient is that they show something of the reproducibility of

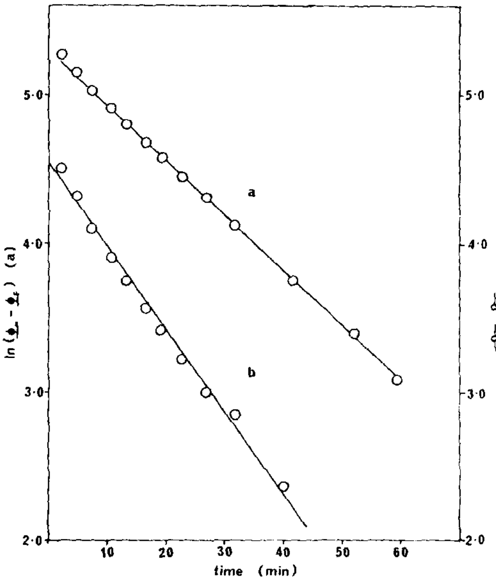

FIG. 1. Plot of a, $\ln(\phi_\infty - \phi_F)$ vs. time, and b, $\ln(d_0 - d_{0_\infty})$ vs. time for the reaction on a 5.0 mg molybdenum film at 0°C.

TABLE 2

Randomization Rates for Benzene and Perdeuteriobenzene at 0°C

Metal	k_F[a]	k_R[a]	k_0[a]	k_6[a]	M_F	M_R	No. of films examined
Rhodium	160	165	90	83	1.8	2.0	12
Iridium	129	118	63	51	2.0 (5)	2.3	10
Molybdenum	32	30	16.6	15.5	1.9	1.9	5
Rhenium	20	18	11	9	1.9	2.0	9
Tungsten	15.2	15.5	8.6	9.0	1.8	1.7	11
Platinum	9.0	9.0	7.7	7.3	1.2	1.2	4
Palladium	3.0	3.0	3.0	3.0	1.0	1.0	4
Tantalum	2.0	2.2	1.0	1.0	2.0	2.2	9
Silver	0.26	0.31	0.14	0.15	1.9	2.1	9
Gold			Inactive				4

[a] Units % μmole min^{-1} (mg-cat.)$^{-1}$.

the results. If a steady state is rapidly achieved for the coverage of the surface by the various adsorbed species, k_0 equal to k_6 and k_F equal to k_R would be expected. Least-squares procedures were used to find the best straight lines. Correlation coefficients were typically 0.998. The results for the reaction at 133 N m^{-2} (1 mm Hg) pressure of reactants and 0°C are shown in Table 2, in descending order of activity.

In addition to the experiments with the benzenes alone, it was also possible to add a suitable pressure of deuterium gas to the mixture at some appropriate point and so determine the rate of exchange with molecular deuterium.

This was done in the cases of platinum and silver, so that comparisons could be made with the work of Anderson and Kemball. The kinetic analysis followed their method, correcting for the initial deuterium content of the benzenes. These results showed that films of these metals prepared by us were of the same order of activity as those of Anderson and Kemball.

Platinum and palladium reacted in a different way from the other metals investigated. The graphs according to Eqs. (1) to (4) were strongly curved, the reaction appearing to reach a different equilibrium point from that expected.

In order to compare metal activities, the initial part of the graph, where linear, gave slopes from which the rate constants quoted have been determined.

The rate of reaction between the benzenes on palladium and on silver was faster than that between benzene and deuterium, while on platinum the reverse is true, as can be seen in Table 3.

Tantalum and silver are of low activity but give a good fit to the kinetic equations used. Gold was found to be inactive in the range 0 to 200°C.

Films of rhodium, silver, and rhenium were prepared in ultrahigh vacuum (10^{-6} N m^{-2}). The rate constants obtained for the reaction on these films were very similar to those obtained when films were deposited at 10^{-4} N m^{-2}. It was found, however, that films deposited at higher pressures than 10^{-4} N m^{-2} were substantially less active.

Discussion

It is surprising that the reaction occurs at all at 0°C over this wide range of metals implying, as it does, the chemisorption of benzene at this low temperature.

TABLE 3

Comparison of Rates of Deuterium Incorporation from Deuterium Gas (k_ϕ) and from Perdeuteriobenzene (k_F) at 0°C

Catalyst	k_F (From perdeuteriobenzene)	k_ϕ (Calculated from Ref. *11*)
Palladium	3.0	0.26
Silver	0.26	0.001 (at +20°C)
Platinum	9.0	23 (at −22.5°C)

Comparison of Metal Activities

The activity series of the metals investigated was Rh > Ir > Mo > Re > W > Pt > Pd > Ta > Ag. This is the same order as that found (in part) by Anderson and Kemball (*11*) for benzene exchange (Pt > Pd > Ag) and for benzene hydrogenation (W > Pt > Pd), and by us for the exchange of toluene with deuterium gas (*9*) (Rh > Mo > W > Pt > Pd).

The activity series found by Schuit and van Reijen (*12*) for the hydrogenation of benzene on silica-supported metals is different (Pt > Rh > Pd), but that found by Amano and Parravano (*13*) is the same (Rh > Pt > Pd). Kubicka (*14*) finds rhenium to be of low activity (Ru > Pt > Tc ≈ Pd > Re) for benzene hydrogenation. It is notable that the results for reaction catalyzed by films show the best agreement.

The plot of the logarithm of the rate constant for the benzene–perdeuteriobenzene reaction against percentage *d* character of the metallic bonds is a reasonably linear relationship. All the results are shown in Fig. 2; the straight line is the least-squares fit, and no allowance is made for the anomalous behavior of platinum and palladium. No correction has been made for any differences in relative surface areas from metal to metal. This dependence of the reaction rate constant on percentage *d* character is similar to the observation of Suhrmann (*15*) that the maximum relative change in electrical resistance of metal films on benzene chemisorption depended on the percentage *d* character.

The data for the third transition series show a clearer relationship. This relationship suggests an electronic effect which can be used to estimate the activity of the metals not represented. We would expect osmium to be of high activity, comparable with iridium, and hafnium to be of low activity. We have not made films of osmium, and hafnium has yet to be examined. We hope to compare the activities of osmium and iridium metal powders.

The absence of ruthenium and osmium prevents reasonable interpretation of the relationship between the logarithm of the rate constant and the position in the periodic table. The maximum rate appears to occur at the Group $VIII_2$ metals, rhodium and iridium.

Mechanism

The randomization reaction is important because it gives information about the chemisorption of benzene at metal surfaces. The technique used is such that the metal and benzene participate in the reaction,

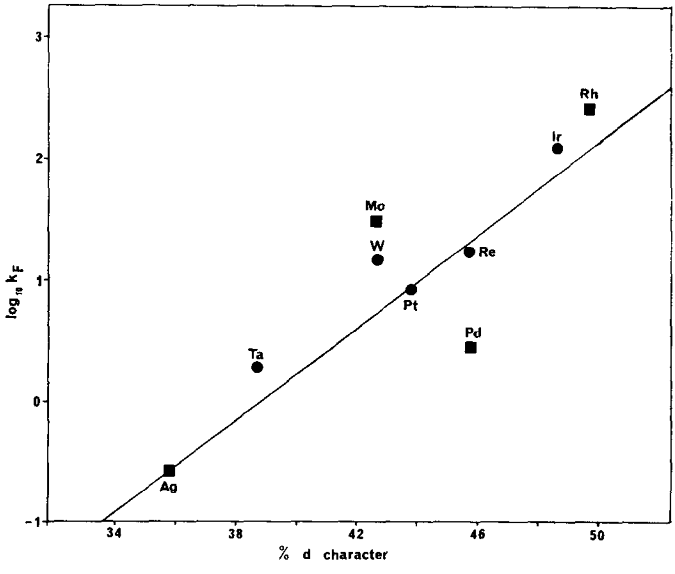

FIG. 2. The dependence of $\log_{10} k_F$ on percentage *d* character of the metallic bonds.

which must occur through intermediates involving associative or dissociative chemisorption of benzene at the surface. The reaction in no way depends upon the presence of molecular hydrogen or deuterium. Three forms of chemisorbed benzene have been suggested, these are shown in Fig. 3(a). Species I and II involve dissociation of the carbon–hydrogen bond and formation of surface-adsorbed hydrogen. It is clear that Species I can give rise to exchanged benzene with the analogous chemisorbed deuterium from perdeuteriobenzene, and that a number of interconversions between Species I and Species II will explain the value of M found to be near 2 in the cases of all metals studied except palladium and platinum.

It is unlikely that any benzene adsorbed as Species III participates in the exchange reaction because, as Harper and Kemball (*16*) have pointed out, this involves hydrogen in two forms, both as chemisorbed hydrogen and as hydrogen present in the gas phase or in a physically adsorbed layer. In the case of exchange with deuterium gas, the associative mechanism suggests the intermediate IV, (Fig. 3(b)) in which the hydrogen at A is directed away from the metal surface while that at B is directed towards it. Reaction at B will not give rise to exchange unless the atom at A can be lost by an Eley–Rideal process (and *vice versa*). Thus, in order that reaction can occur by this associative mechanism, *two* forms of adsorbed hydrogen must be present, one of which is not strongly bound to the surface. It seems unlikely that in a system which does not contain added hydrogen, sufficient hydrogen molecules could be present to make this mechanism possible.

Anderson and Kemball (*11*) noted a poisoning of the exchange reaction on palladium catalysts which they attributed to cyclohexane which competed with benzene for the surface. They did not observe any poisoning of the exchange reaction on platinum. The similarity between our results on platinum and palladium and those of Anderson and Kemball leads us to suggest that the poisoning agent in our case is the same as theirs, and that on platinum it can be removed by the excess deuterium present. It would thus seem to be formed at some earlier stage in the hydrogenation process, possibly as a π-cyclohexenyl surface complex similar to the π-cyclohexenyl palladium chloride dimer which has been reported (*17*). In the case of the benzene–perdeuteriobenzene reaction this intermediate is formed and poisons the reaction, but no excess deuterium is present. This resuscitates the view that the exchange and hydrogenation reactions are two different processes occurring through different intermediates, and in this case the hydrogenation intermediates poison the exchange reaction. This supposition is further strengthened by Rooney and Webb (*18*), who have accounted for the readier activity of palladium and platinum as catalysts for the hydrogenation of benzene in terms of their ability to form metal-benzene π-complexes. Anderson (*19*) has reported similar poisoning of the hydrogenation reaction in the case of tungsten films, but we do not observe poisoning of the benzene–perdeuteriobenzene reaction on this metal. The comparison between the exchange rates of benzene with deuterium and perdeuteriobenzene is interesting. Very large differences indeed, by a factor of 10 or more,

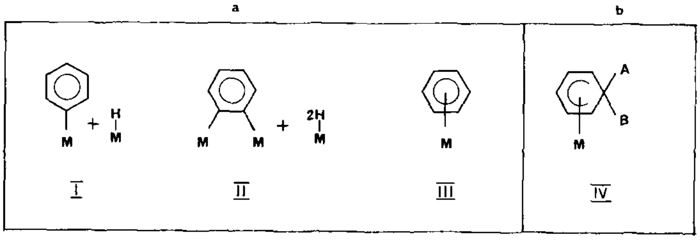

FIG. 3. Reaction intermediates formed on the chemisorption of benzene at metal surfaces.

are observed between the values of k_F and k_ϕ (Table 3).

The observed difference of rates, in the case of palladium and silver, could be interpreted if one assumes that benzene is present on the catalyst surface as dissociatively and associatively adsorbed molecules, respectively responsible for the exchange and deuteration reactions. In the presence of gaseous deuterium, the concentration of the cyclohexadienyl radicals is expected to increase at the expense of the phenyl radicals and the exchange rate to decrease simultaneously. Such an interpretation, however, cannot be valid in the case of platinum, since both reaction rates are similar.

It is possible that the intermediate IV (Fig. 3) could react with gaseous, or physically adsorbed perdeuteriobenzene giving rise to dissociatively adsorbed perdeuteriophenyl and exchanged benzene. It seems likely that both associatively and dissociatively adsorbed species are present on all of the metals except gold, but that the dissociatively adsorbed species is the reactive one. Reference to the extensive literature of organometallic compounds gives no help, since the large number of σ-bonded aryl compounds (*20*) is matched by the almost equally large number of bis-π-arene complexes (*21*)!

The reaction does not occur on gold, and this can be explained by the lack of *d* character in the metallic bonds. This in turn suggests that benzene will not be dissociatively chemisorbed at the gold surface. Alternatively it is possible that our gold films are of low surface area and the rate may, in consequence, be too slow to measure.

The elements of the first transition series are being studied, and our findings will be presented in a future publication. In general, the trends shown in this study are also found in the first series.

The metal activity information would be more useful if relative surface areas of the metal films were known. A study of the relative surface coverage of different metal films by radiochemical means is in progress.

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