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The Exchange with Deuterium and Deuteration of Benzene on Evaporated Palladium–Gold Alloy Films

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The activity of characterized Pd–Au alloy films for deuteration of benzene and hydrogenation of *p*-xylene falls to zero at median alloy compositions. Activity for the exchange reaction between benzene and deuterium persists to the Pd-lean compositions, in agreement with a brief report by Horrex *et al.* (*5*), but rates are much reduced (by 10^2–10^3) compared to those found with Pd-rich films. These findings are consistent with a dissociative mechanism for the exchange reaction. The *trans/cis* ratio of 1,4-dimethylcyclohexanes formed in *p*-xylene hydrogenation does not vary significantly with alloy composition suggesting that the probability of "roll-over" of cyclohexene intermediates is not appreciably affected by Au content.

INTRODUCTION

There has been considerable debate as to the mechanisms of exchange of deuterium with, and addition of deuterium or hydrogen to, benzenoid hydrocarbons (*1–6*). In particular, a clear decision is awaited as to whether exchange proceeds by a dissociative or by an associative mechanism and in the hydrogenation of dialkylbenzenes there is doubt as to the route whereby *trans*-dialkylcycloalkanes are produced (*2*, *7*). Horrex, Moyes and Squire (*5*) have reported briefly a persistence of exchange activity for ring hydrogens in toluene to alloys of low palladium content in the Pd–Au series whereas deuteration activity disappears at about 60 at.% gold. We felt that this result was of special interest for the exchange mechanism and that a study of the benzene/deuterium reaction on well-characterized Pd–Au alloy films was desirable. Such alloy film catalysts were available as a result of previous work in this laboratory (*8*). This paper describes in addition a short study of *p*-xylene hydrogenation on a similar series of Pd–Au films.

EXPERIMENTAL METHODS

Alloy film catalysts were prepared as previously described (*8*). Essentially the technique is one of simultaneous evaporation of the component metals from approximately point sources positioned at the center of a spherical Pyrex reaction vessel of 11.2 cm diam. The vessel wall was maintained at 450°C during deposition and also during a subsequent 1 hr anneal in 2–3 Torr of deuterium. The deuterium was removed by brief pumping at about 100° before admission of the reaction mixture. Film weights were in the range 20–60 mg. The previous study has demonstrated the films to be homogeneous over their lateral extent and also on a microscale. Lateral homogeneity to within 4–5% was further confirmed in the present work by atomic absorption spectrometric analyses; further, the validity of estimating alloy compositions from source-filament weight loss was confirmed to within the same limits. Because of the small surface area and severely sintered condition of these films they are less active than other more usual forms of catalyst used in fundamental work. Activity of the films was independent of their weight and, accordingly, the surface area has been assumed to be equal to the apparent geometric area.

For studies of the benzene/deuterium reaction an A.E.I. MS10 mass spectrometer was connected via a capillary leak to the 650 ml reaction vessel. About 3% of the contents of the vessel was removed per hour permitting continuous analysis. Electrons of 12.5 Volt energy were used in the analysis and fragmentation due to loss of one "hydrogen" atom was 3.4% for benzene and 4.3% for cyclohexane. Masses 77 to 96 were measured. Customary corrections for the relative sensitivity of benzene and cyclohexane in the mass spectrometer (2.7 to 1.0), natural isotopic abundance and fragmentation were applied to peak heights.

Reaction rates were measured in the *p*-xylene hydrogenation experiments by *in situ* glc analysis. A small quantity (about 1%) of the contents of the reactor was removed periodically and diverted to the chromatographic column using standard instrumentation. Silicone SE30 supported on Chromosorb W was used as stationary phase in a 6 ft × $\frac{5}{16}$ in. diam. column operating at 65°. Peak areas were taken as a direct measure of concentration of the hydrocarbons present.

In benzene/deuterium runs a mixture containing 0.72 Torr of benzene and a 15-fold excess of deuterium was admitted to the vessel at a temperature of 20°, giving 1.52×10^{19} molecules of benzene initially present. Reaction temperatures were in the range 80 to 250°. For xylene hydrogenation a mixture containing 1.06 Torr of *p*-xylene and a 20-fold excess of hydrogen was expanded into the reactor at 100° which was the single temperature chosen to study this reaction. Thus there were initially 1.78×10^{19} molecules of xylene present. At least six alloys of different composition were used for each study and an identical procedure was followed in each case.

Materials. "Analar" benzene, said to contain less than 3 ppm of thiophene and other sulfur-containing impurities was passed successively through activated (B.A.S.F.) BTS catalyst and Linde 5A molecular sieve. The *p*-xylene (>99.5% pure) was a gift from I.C.I. Ltd. Hydrocarbons were subjected to freeze–thaw cycles *in vacuo* before use. Hydrogen (or deuterium) was palladium diffused.

RESULTS

Benzene Exchange and Deuteration

The identification of the various reaction species on the basis of masses of the ions observed was unequivocal for all compounds except d_6-benzene and d_0-cyclohexane, which have the same mass. However, the almost complete absence of any ions in the mass range 85 to 89 indicated that cyclohexanes containing 1 to 5 deuterium atoms were not being formed, and it was therefore justifiable to assume that d_0-cyclohexane was absent and that all the ions of mass 84 were due to d_6-benzene. Deuteration was observed only with the alloys of composition 100, 83, and 62 at.% Pd. No cyclohexanes were formed on the remaining alloys even when the temperature was raised to 250°. Exchange, on the other hand, occurred on all alloys, although higher temperatures were needed when the palladium content of the alloys was reduced below about 50 at.%. Pure gold was inactive for exchange within the temperature range studied but a very small exchange activity was observed at about 320°. In those cases where both exchange and deuteration were occurring, the activity for deuteration was generally substantially lower than activity for exchange. Further, it was found, in agreement with the observations of Anderson and Kemball (*1*), that the total percentage of cyclohexanes increased linearly with time, implying that the deuteration reaction is zero order with respect to the pressure of benzene.

Activation energies and frequency factors for deuteration (and for exchange: see below) were obtained from rates measured using the same reaction mixture at three temperatures because the mass spectrometer made possible the accurate measurement of very slow rates with little conversion of reactants. Thus, all measurements were gen-

TABLE 1

ACTIVATION ENERGIES AND FREQUENCY FACTORS FOR BENZENE DEUTERATION (E_c, A_c) AND EXCHANGE (E_b, A_b)

Alloy composition (at.% Pd)	E_c (kcal mole^{-1}) ± 0.5	$\text{Log}_{10} A_c$ (A_c in molecules cm^{-2} min^{-1})	E_b (kcal mole^{-1}) ± 0.5	$\text{Log}_{10} A_b$ (A_b in molecules cm^{-2} min^{-1})
100	5.1	17.4	19.0	25.8
83	4.3	16.2	16.2	23.5
62	6.8	17.2	17.9	23.7
38	—	—	21.6	24.0
32	—	—	20.1	23.1
18	—	—	17.0	21.2

erally completed within a decrease in % d_0-benzene from 100 to about 88. Reproducibility of rates was satisfactory with several 100% Pd films and some corroboration that a stationary state existed in reactions with all films lay in the finding of consistent course kinetics (deuteration, zero order; exchange, first order) at each temperature. Plots of $\log_{10} k_c$ (where k_c is the rate of deuteration) against $1/T$°K were linear and derived parameters are given in Table 1. The initial distribution (*1*) of deuterocyclohexanes for each film is shown in Table 2, in which an attempt is also made to show the effect of temperature by giving initial distributions at the second temperature of reaction (generally measured at 6–10% conversion of d_0-benzene).

Following Anderson and Kemball two different rates may be defined for the exchange reaction. The first of these is the rate of entry of deuterium into the benzene. In any exchange reaction, this rate can be obtained from a function which is a measure of the total deuterium content of the products. In this case ϕ was defined by the equation

$$\phi = u + 2v + 3w + 4x + 5y + 6z,$$

where u to z represented the percentage of total benzene present as d_1–d_6-benzene. In an exchange reaction which is not complicated by side reactions the variation of ϕ with time is given by

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

where k_ϕ is the initial rate of entry of deuterium atoms into 100 molecules of the d_0 compound and ϕ_∞ is the final value corresponding to equilibrium. In this work, because a 15/1 ratio of deuterium to benzene partial pressures was used, ϕ_∞ had a value of 500.

Following Anderson and Kemball (*1*), an analogous equation to (1), of practical usefulness, was used to describe the rate of disappearance of d_0-benzene where k_b is the rate constant and b_∞ the percentage benzene corresponding to equilibrium in the ex-

TABLE 2

INITIAL DISTRIBUTIONS OF DEUTEROCYCLOHEXANES

Alloy composition (at.% Pd)	Temp (°C)	$C_6H_6D_6$	$C_6H_5D_7$	$C_6H_4D_8$	$C_6H_3D_9$	$C_6H_2D_{10}$	C_6HD_{11}	C_6D_{12}
100	86	7	7	11	10	12	17	35
	100	4	4	8	8	17	20	40
83	86	6	9	9	9	11	15	42
	106	4	1	3	3	5	18	66
62	110	—	—	—	—	—	22	77
	122	—	—	—	—	1	13	86

change. b_∞ was taken as zero on account of the large excess of deuterium used.

Plots of $\log_{10}(\phi_\infty - \phi)$ against time and also of $\log_{10}(b - b_\infty)$ against time were found to be linear in all cases. Anderson and Kemball, having obtained curved lines for corresponding plots with palladium film catalysts, reasoned that the effect was due to lessening in overall rate of the exchange reaction caused by the increasing amount of cyclohexane, and modified the equations accordingly. In the present work measurements were taken in general at much lower degrees of conversion of benzene and the total amount of cyclohexanes present at any time was never greater than about 4%. On the 100% Pd film, which was the most active for both exchange and deuteration—and on which, therefore, the consumption of benzene was greatest—a slight departure from linearity was observed at the third temperature of reaction for the $\log_{10}(\phi_\infty - \phi)$ against time plot. However, the effect was slight and it was not considered necessary to modify the rate equations. Values of k_ϕ and k_b are readily calculated from the linear plots and the ratio of these two rates $k_\phi/k_b = M$ represents the mean number of deuterium atoms entering each benzene molecule which underwent exchange in the initial stages of the reaction (Table 3, col. 9). Initial distributions of deuterobenzenes, obtained from individual rates of production, are given in Table 3, cols. 3–8: here also an attempt is made to show the effect of temperature by including a second "initial" distribution measured while the overall conversion of d_0-benzene increased to not more than 8–12%. The deuterobenzene distribution obtained by Anderson and Kemball with a high-area Pd film at 29.5° is included for comparative purposes. Plots of $\log_{10} k$ against $1/T$°K, which were in general linear (Fig. 1), permitted estimates of Arrhenius parameters for the exchange reaction (Table 1).

p-Xylene Hydrogenation Experiments

Under the experimental conditions detailed earlier, *p*-xylene was hydrogenated at a measurable rate to yield a mixture of *cis*- and *trans*-1,4-dimethylcyclohexanes. Both are initial reaction products because it was verified separately that no *cis–trans* isomerization of the dimethylcyclohexanes occurs at 100° on these films. Activity declined steadily from the value for pure palladium through the palladium-rich alloy compositions and no activity was detected for alloys of less than 50–60 at.% Pd. The ratio of *trans* to *cis* products remained constant during the course of each reaction. There was a small and reproducible difference between the value of this ratio for pure

TABLE 3

INITIAL DISTRIBUTIONS OF DEUTEROBENZENES FOR THE EXCHANGE REACTION

Alloy composition (at.% Pd)	Temp (°C)	C_6H_5D	$C_6H_4D_2$	$C_6H_3D_3$	$C_6H_2D_4$	C_6HD_5	C_6D_6	$M = k_\phi/k_b$
100	86	84	8	3	3	—	3	1.35
	100	80	14	3	2	1	1	1.22
83	86	96	4	—	—	—	—	1.17
	106	85	9	2	2	—	1	1.19
62	110	93	5	—	—	—	2	1.15
	122	86	7	2	3	1	2	1.28
38	198	75	4	2	1	1	16	1.75
	216	73	8	2	3	2	12	1.75
32	213	80	7	2	2	2	8	1.64
	234	77	12	2	3	2	5	1.37
18	207	86	5	3	2	—	4	1.29
	226	79	8	3	3	2	4	1.55
100(1) (unsintered)	29.5	62	18	7	4	3	6	

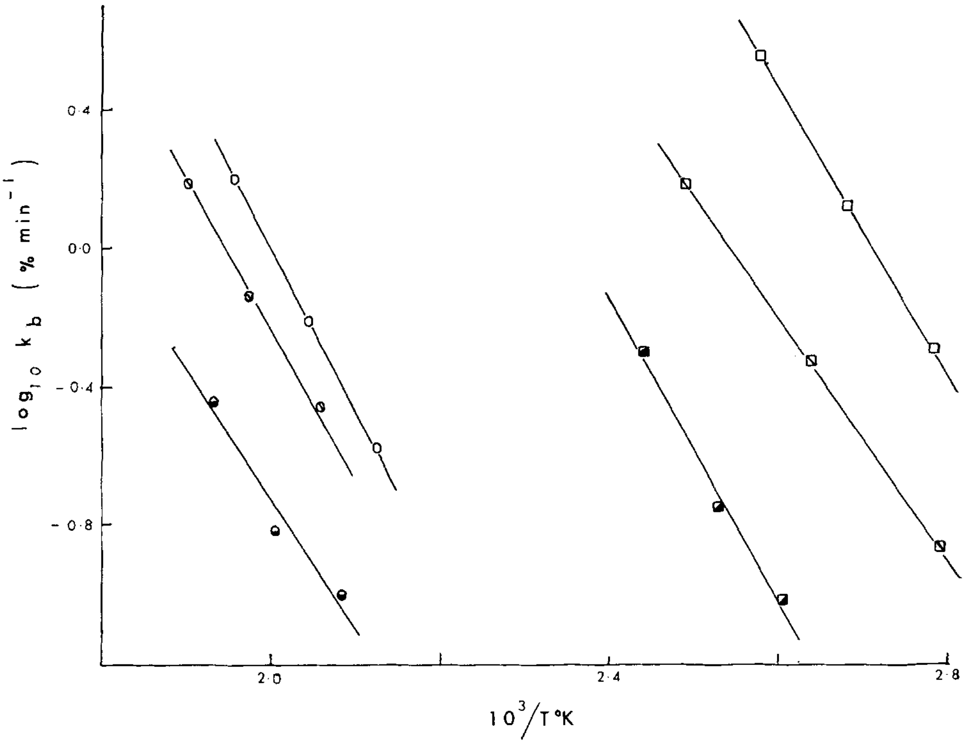

FIG. 1. Arrhenius plots for benzene exchange. Alloy compositions in at. % Pd: □ 100, ▧ 83, ◪ 62, ⊘ 38, ○ 32, ◒ 18.

palladium and its value for the active alloys. Table 4 summarizes the results.

DISCUSSION

Mechanisms of Exchange and Deuteration of Benzene

It has not yet been clearly established whether benzene undergoes exchange on transition metal surfaces by a dissociative or an associative mechanism. The former route, the normal mode of exchange of alkanes, was discussed by Anderson and Kemball (*1*) and has been enlarged by the proposal (*3*) that π-aryl species are the precursors of σ-phenyl radicals. A clear molecular analogy to the reversible dissociative attachment of a benzene ring to a single metal-atom center exists (*9*). The associative scheme in its preferred form received its main impetus from the mechanism developed by Rooney, involving *trans* addition/elimination of hydrogen atoms with π-allylic species, to explain *inter alia* multiset exchange of cyclic alkanes (*10*). This impetus may have been partly removed by recent work by the same group (*11*), which demonstrates instead the operation of a "roll-over" mechanism in such reactions. Clear organometallic analogies remain for π-cycloalkadienyl groups bonded at single metal atoms, and, at least, these

TABLE 4

ACTIVITIES AND *trans/cis* RATIOS OF PRODUCTS FOR *p*-XYLENE HYDROGENATION AT 100°C

Alloy composition (at.% Pd)	Activity (% min^{-1})	*trans/cis*
100	0.327	2.12
93	0.290	1.45
82	0.153	1.51
63	0.063	1.70
61	0.067	1.60
47	—	—
40	—	—
20	—	—
0	—	—

are likely to be relevant for the hydrogenation/deuteration reaction.

Much interest has centered around the effects of substituents on exchange reactivity of benzenoid ring hydrogens and the "ortho deactivation effect" has been cited by Garnett and Sollich-Baumgartner as strong evidence for a dissociative route (*3*). Harper, Siegel and Kemball (*4*) have argued, however, that the effect does not unequivocally establish the dissociative mechanism. They found also that the ratio of exchange to deuteration was largely unaltered from benzene to *p-tert*-butylbenzene on platinum, palladium and nickel, but on tungsten the ratio was increased by about 300 leading to their tentative conclusion that exchange can proceed by different mechanisms on different metals.

Exchange and Deuteration on Palladium–Gold Films

The present results for well-characterized Pd–Au alloy catalysts offer an opportunity to consider the exchange problem further. Activity for exchange persists, albeit much reduced (by 10^2–10^3) on alloys of low Pd content (Fig. 1) and deuteration activity disappears at less than about 50 at.% Pd (Table 1: see also Fig. 2). If exchange takes place through an associative intermediate at the low Pd compositions we may ask, following Burwell in a similar connection (*12*), why does not this species add on another deuterium atom?

It has been recognized that different mechanisms might operate on different metals (*4*) and it seems reasonable to infer that instances of exchange without deuteration imply that the dissociative exchange route operates. Reports of exchange activity unaccompanied by deuteration on copper and silver at temperatures in excess of 300° with low pressures of hydrocarbon (*1*) may not, however, be taken as examples of this effect: the investigators concerned stress that the deuteration was thermodynamically disfavored under their experimental conditions. Apart from the preliminary finding by Horrex, Moyes and Squire (*5*), the present results for the three Pd-lean alloy films provide a first clear example of a fundamental difference existing between the two reactions on surfaces where both can, in principle, take place because deuteration is feasible thermodynamically at 200° under the experimental conditions. This suggests strongly, therefore, that the small exchange activity at low Pd contents derives mainly from a dissociative mechanism. There is likely to exist a sharp increase in rate of exchange by the dissociative route for Pd contents greater than about 50 at.%, by analogy with results for methane–deuterium exchange (*13*)—necessarily dissociative in character. It cannot be decided on the basis of the present results whether, and to what extent, an associative mechanism contributes to exchange at Pd contents greater than about 50 at.%. The findings of Harper, Siegel and Kemball (*4*), already referred to, for comparative exchange and deuteration of benzene and *p-tert*-butylbenzene on Pt, Pd, Ni, and W, prompt caution in excluding a contribution from this mechanism.

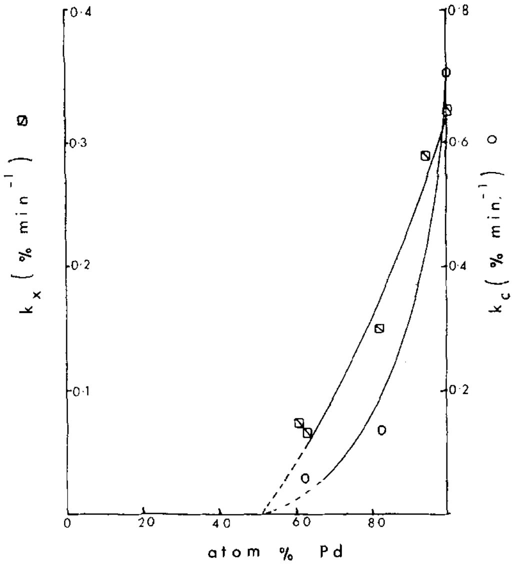

FIG. 2. Rates of benzene deuteration at 112° (k_c) and of *p*-xylene hydrogenation at 100° (k_x). The Au-rich alloys, which showed no measurable activity for either reaction (see text), are omitted.

While it is clear that a composition of about 50 at.% Pd represents a turn-around point* for both deuteration and exchange, two points of interest remain. The persistence of activity for the exchange of benzene compared to the disappearance of activity in methane exchange in low Pd alloys may arise, in part, because metal–phenyl bonds are stronger than metal–alkyl bonds *(15)* leading to more rapid dissociation of benzene. However, as has been strongly argued *(3)*, both dissociative chemisorption and the reverse step are facilitated for benzene by the ability of a benzenoid carbon atom to expand its covalency. This feature can, it seems, partly compensate for the absence of *d* vacancies in alloys of less than about 50 at.% Pd. The suggestion *(16)* that some reactants may have a decisive influence electronically on the "active" metal atoms in binary alloys may be relevant. The $d\pi$ component in metal–phenyl bonds *(17)* provides a means by which electronic charge can be withdrawn from the metal. This may allow *d* vacancies to be generated in a Pd-lean alloy surface which can assist in the deuterium substitution step. Even then, 100% Au films show no activity for the exchange reaction below 320° whereas all the alloys are active at 200°, and this reinforces the belief that the rigid band model for binary alloys such as Pd–Au is too imprecise to provide an interpretation of all the catalytic observations.

The rigid band model has now been experimentally demonstrated to be a crude approximation for the analogous Pd–Ag system *(18)* from (i) a reliable determination of the number of *d* holes in pure Pd (0.36 rather than 0.60 as long assumed from the disappearance of paramagnetism at more than 60 at.% Ag) and (ii) an anomalously high thermoelectric power for a 1% Pd alloy which indicates a high density of states (which are therefore *d*-like) just below the Fermi level. A qualitative description of the catalytic behavior of Pd–Au alloys may be attempted in terms of Friedel's model of impurity solute atoms in metallic solution which has proved useful for several alloy systems *(19)*. Thus, at low Pd contents, while the lower nuclear charge of the Pd atom will be "antiscreened" by a reduction in the *s–p* electrons in the Pd cell, the centroid of the 4*d* levels on the Pd may still be expected to rise by several volts to above the corresponding level for Au.† *d* Vacancies sufficient to allow some dissociative adsorption of benzene (but not, apparently, deuteration) may be produced by electron promotion from these raised states to the Fermi surface *(20)* with a smaller energetic cost than in pure Au. Of particular interest are Mössbauer determinations of electron shift between Pd and Au sites *(21)*. These show that in Au-lean alloys the electron density at the Au nucleus is about 30% greater than in pure Au on account of the difference in attractive potential of the two kinds of atom, and not less as would be expected if *s* electrons from Au sites filled the Pd *d*-band. It has been suggested *(22)* that the depression of the Pd *d* states below the Fermi energy on Au addition (so that Pd *d* holes fill at the expense of Pd *s* electrons) is a direct consequence of the descreening of the Pd nuclear charge.

Surface Ensembles

In a recent approach Dowden has suggested *(23)* that nearest, and possibly next-nearest, neighbors at the surface may exert the predominant modifying influence electronically on a Pd site atom. The relevant "ensemble" of metal atoms (in, for example, a Pd–Au solution) within which a *d* vacancy remains or is filled, comprises a different number of atoms at different crystal planes.

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* The presence of sorbed hydrogen or deuterium may cause the alloys to behave electronically as though they contained more Au than their nominal composition would suggest. Published isotherms *(14)* suggest that $PdH_{0.1}$ represents a maximum possible "hydrogen" content in this work and this may determine that the break in activity, estimated by extrapolation (Fig. 2), is at about 50 at.% Au in *p*-xylene hydrogenation rather than at 55–60 at.% at which paramagnetism falls to zero in this alloy series.

† Note added in proof: Spectroscopic studies *(28)* suggest that the top of the Pd *d* band is about 1 eV higher than that of the Au *d* band.

The general result of the main assumption, however, is that the number of d-vacancy bearing surface sites is predicted to vary in a more gradual manner with change in alloy composition than the simple d-band model suggests. Some features of the present results appear also to find a satisfactory interpretation on this basis. Firstly, the activity variation for exchange tends to be contained more in the frequency factor than in the activation energy (Table 1). Secondly, the persistence of a small exchange activity in Pd-lean alloys (essentially removed at 100% Au) is understandable on this view; the attendant inactivity for deuteration (or hydrogenation) may reflect the electron-donating nature (*24*) of the intermediates in this reaction whereby the filling of surface d vacancies tends to be assisted.

Initial Distributions of Deuterobenzenes and Deuterocyclohexanes

The initial distributions of deuterobenzenes and the derived values of M (Table 3) indicate that exchange did not occur entirely by replacement of one hydrogen atom at a time, although such simple exchange was clearly dominant. The small amount of multiple exchange, which increases with temperature, and which may result from either phenyl $\rightleftharpoons$ phenylene (*1*) or π-aryl $\rightleftharpoons$ phenyl (*3*) interconversions is similar to the finding of Anderson and Kemball (*1*) for an unsintered Pd film. In contrast, however, to their findings d_{12}- and d_{11}-cyclohexanes were dominant (Table 2). Thus, in the present experiments, final saturation appears to be preceded by repeated roll-over (see below) of cyclohexenes at the surface. Deuterobenzenes may, in principle, be formed by the same route (omitting the final saturation) by a reversal of the steps by which "hydrogen" atoms are added to the ring followed by benzene desorption. It appears, however, from the generally small deuterium number of the exchanged benzene that this mechanism does not make a substantial contribution except perhaps with the Au-rich alloys where the higher reaction temperatures encourage benzene desorption.

Hydrogenation of p-Xylene

Cis products normally predominate in transition-metal catalyzed hydrogenations of disubstituted benzenes. Palladium catalysts are particularly effective, however, in forming the thermodynamically more stable *trans* products. The results of Table 4 illustrate again their exceptional ability in this regard. A mechanism involving *trans* addition of hydrogen atoms to chemisorbed hydrocarbon cannot be excluded, as indicated earlier. However, the absence otherwise of an unambiguous example of such *trans* addition coupled with the demonstration (*11*) of repeated "roll-over" of olefin prior to its saturation on palladium catalysts supports the mechanism originally put forward by Siegel (*25*) to explain formation of *trans* product. Since transient desorption of an intermediate cyclohexene is a necessary preliminary to *trans*-dimethylcyclohexane production, whereas the *cis* isomer may, in principle, be produced additionally in one step, a change in one of the experimental variables might favor one product rather than the other. Siegel and Smith (*26*) have indeed observed that increased hydrogen partial pressure in 1,2-dimethylcyclohexene hydrogenation caused a decrease in the *trans/cis* ratio in the product and they concluded that final saturation of olefin was encouraged, in competition with desorption, at higher hydrogen pressures. The present results (Table 4) show that the first addition of Au to Pd produces a small reduction in *trans/cis* ratio, possibly reflecting a texture change (*8*), but subsequent additions have no further effect stereochemically, suggesting that the probability of "roll-over" is insensitive to Au content. It would be of interest to test this conclusion by a study of the relative rates of one-set and two-set (*27*) exchange of cyclohexane at the same alloy compositions.

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