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Catalytic Deuterium Exchange Reactions with Aromatics VI. Studies in Platinum Catalyst Reproducibility and Activation Procedures

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Factors influencing the activity, reproducibility, and stability of reduced platinum oxide as a catalyst in exchange reactions between deuterium oxide and organic compounds have been investigated. Two effects may be distinguished which are associated with (*i*) prereduction and activation procedures of the catalyst *prior* to exchange and (*ii*) deactivation of catalyst by reagents *during* exchange. Variables which influence process (*i*) include temperature, water, hydrogen pressure, and rate of hydrogen addition. Present results show that these factors may produce catalysts differing by 600% in activity, however, catalyst reproducibility of ±2% can be achieved by careful control of such variables. In process (*ii*) deactivation by benzene at 38.8°C of a hypersensitive catalyst has the effect of doubling the activation energy of benzene–deuterium oxide exchange. ($E'_a = 9.6 \pm 0.5$ kcal/mole, $E''_a = 19 \pm 1$). This is partly offset by a compensation effect ($\log_{10} A' = 23.6 \pm .4$, $\log_{10} A'' = 29.1 \pm .7$) which is attributed to a modification of catalyst sites by *π-complex* interaction with the catalyst surface. Deactivation is initially faster and more reproducible in the presence of a mixture of water and benzene, than deactivation by benzene alone. A similar result is obtained with a 0.36 mole % solution of anthracene in benzene. The relatively high E_a values suggest that diffusion processes are not rate-determining. Deuterium distributions in the labeled benzenes were measured and found to vary with the method of catalyst preparation. Distribution studies indicate that both multiple and stepwise processes are involved in the deuteration mechanism of benzene.

INTRODUCTION

Extensive studies of platinum-catalyzed exchange reactions between heavy water and organic compounds have already been reported (*1–4*). The procedure yields a convenient source of deuterated solvents and intermediates for NMR and mass spectrometry (*5*) and tritiated compounds for tracer work (*6, 7*). A chemisorption theory involving π- and σ-complexes has been proposed to account for the observed reactivities (*2, 3, 8*). In order to examine this proposed charge transfer mechanism more thoroughly, a detailed study of the reaction has been performed (*9*). For this purpose it was necessary to develop improved methods of catalyst activation (reduction of platinum oxide), which would yield catalysts possessing suitable activity and high reproducibility.

A critical evaluation of various methods used for the preparation of active platinum as a catalyst for exchange reactions is outlined in this paper. This study is confined to the activation of platinum, since preliminary experiments indicate that this catalyst is the most active of the transition metals for exchange experiments of the type previously reported (*9*). Techniques for the preparation of platinum black with reproducible surface areas have already been described (*10*); however, previous experience has shown that further refinements in catalyst preparation are necessary if these catalysts are to be used for kinetic studies in exchange reactions.

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EXPERIMENTAL

Exchange techniques were the same as described in earlier publications (*3*, *4*). For all reactions, unless otherwise stated, the system used was the exchange between benzene and deuterium oxide for several reasons. Firstly, benzene exchanges rapidly at low temperatures (32°C), while the equivalence of its ring positions permits a simple kinetic description in terms of only one rate constant. Secondly, this compound is an ideal example of a π-electron system and is thus eminently suitable for examining a π-complex theory of catalysis (*2*, *8*, *11*).

A measure of catalyst activity was obtained by calculating the first order rate constant, k, as defined by the equation

$$dD_t/dt = k[(D_\infty - D_t)/D_\infty] \quad (1)$$

where D_∞ and D_t are the deuterium contents of benzene at equilibrium, and after time t, respectively.

Integrating Eq. (1) and rearranging:

$$k = -(2.3D_\infty/t) \log [(D_\infty - D_t)/D_\infty] \quad (2)$$

Direct comparisons of catalytic activity were only made between catalysts coming from the same prereduced stock.

Deuterium oxide (99.75% isotopic purity) was obtained from the Australian Atomic Energy Commission. Platinum oxide was supplied by Matthey Garrett Pty. Ltd.

RESULTS AND DISCUSSION

Pretreatment of Catalyst—Prereduced Catalyst Stock

The simplest and most rapid method of reducing *dry* platinum oxide ($PtO_2{\cdot}2H_2O$) is by exposure to hydrogen gas. For low pressures of hydrogen (5–15 cm), the reaction is extremely slow and not easily controlled, due to a long induction period. When the pressure of hydrogen is increased to approximately 20 cm, a critical value is reached where the reduction proceeds explosively and the extremely high temperatures generated during the reaction result in an almost complete loss of catalytic activity.

A satisfactory reduction rate is achieved at a hydrogen pressure of 1 atm if the platinum oxide is moistened with water prior to hydrogen exposure, thus ensuring that hydrogen diffusion through the aqueous layer becomes the rate-determining step in the process. Depending on the amount of water used and the extent to which the system is agitated, reduction is usually completed within 48 hr at 30°C. The resulting catalyst, although of very high activity, possesses poor reproducibility, since up to 100% variations are observed in the first order rate constant for the benzene–deuterium oxide exchange.

From these initial studies, it was decided to prepare a large batch of reduced catalyst stock by exposing moistened platinum oxide to hydrogen, then to equilibrate with the atmosphere and examine the most satisfactory methods for activating this reduced, oxygen-poisoned stock. The following general method (Procedure A) for the preparation of prereduced stock was used: Platinum oxide, sufficient for 50 individual exchange reactions, was reduced with hydrogen (1 atm pressure) in the presence of water (3 times weight of oxide) until reduction was completed, the water pumped off to 0.06 mm at 120°C, and hydrogen reintroduced at a slow rate (3 cm/min) at 30°C until reduction was complete. Any adhering water was pumped off at 30°C and the catalyst equilibrated with the atmosphere.

Activation of Prereduced Catalyst Stock

Various techniques for activating samples of this prereduced catalyst stock were investigated, the activities being checked by performing exchange reactions with benzene and heavy water at 32°C in the following manner. Prereduced catalyst stock (20–30 mg) was activated in an ampoule by one of the methods outlined below, residual hydrogen pumped off (0.06 mm) after activation, the ampoule vacuum-sealed and placed in a reaction vessel containing the necessary quantities of benzene and heavy water to maintain constant water-to-catalyst and benzene-to-catalyst ratios of 48 and 63, respectively (equilibrium deuterium content 50%). The reactants were then deaerated by successive warming and freezing, the reaction tube vacuum sealed (0.06

mm), the reagents permitted to reach reaction temperature in a water bath, and reaction commenced by breaking the seal of the catalyst ampoule. The reactor was shaken to prevent diffusion from becoming rate-determining, however, this tendency was small for reactions occurring at 32°C. Experiments also indicated that reduced platinum oxide is sensitive to oxygen at room temperature whereas nitrogen, carbon dioxide, and contamination of reactants by silicon grease had negligible effect.

TABLE 1
RESULTS OF CATALYST ACTIVATION PROCEDURES

Run	Temperature (°C) of		Cat.[b] stock	% D in Benzene	Reaction time (hr)	k (% D hr^{-1})
	Catalyst activation	Hydrogen[a] evacuation				
1a	30	30	C	4.8	1.5	3.54
1b				7.5	1.5	5.50
2a	100	100	C	6.0	1.5	4.30
2b				7.5	1.5	5.50
3a	100	100	C	4.3	1.5	4.0
3b				6.6	1.5	4.82
3c				5.1	1.5	5.54
4a	100	100	C	2.0	1.5	1.38
4b[c]				3.5	1.5	2.45
5a	−90	100	C	13.5	1.5	10.06
5b				15.5	1.5	12.4
6	−196	−196 then 30	C	0.0	1.5	0.0
7a	−90	−90 then 30	D	28.5	8.0	5.32
7b			D	29.0	8.0	5.43
8[d]	−90 then 30	30	D	27.5	16.0	2.50

[a] All catalyst ampoules were evacuated to pressures of 0.06 mm except Runs 3a, b, and c where effect of residual chemisorbed hydrogen was investigated. In tubes 3a, b, hydrogen pressure was 1 mm while in 3c it was 5 mm. Reagent/catalyst weight ratios are 48 and 63 for water and benzene, respectively.

[b] Differences in catalysts C and D are that they originate from differently prereduced stock.

[c] Catalyst exposed to 300°C for 1.0 hr subsequent to activation.

[d] Catalyst activated first at −90°C for 12 min, then exposed for further 12 min to H_2 at 30°C.

The results of the various methods used to activate the prereduced catalyst stock are reported in Table 1. The simplest activation procedure involves 1 atm of hydrogen at room temperature for a period of 12 min, excess hydrogen pumped off (0.06 mm), the catalyst ampoule sealed, and used for the exchange reaction. Results indicate that a highly active catalyst but one of poor reproducibility is obtained (Runs 1a and 1b). Preliminary results show that residual, chemisorbed hydrogen has no significant effect on catalyst activity or reproducibility (Runs 2 and 3) as does a change in the temperature of activation from 30° to 100°C. Lack of reproducibility may be caused by sintering of the catalyst during the activation process, despite the fact that this reaction is markedly less exothermic than the reduction of unreduced platinum oxide (Procedure A). However attempts to increase catalyst reproducibility at the expense of activity by subjecting the catalyst to further sintering were unsuccessful (Run 4).

Sintering during the activation process was therefore avoided by room-temperature evacuation of the ampoule containing the prereduced catalyst stock, until all traces of water were removed, then exposing the catalyst to 1 atm of hydrogen at −90°C in a Dry Ice-acetone bath for 12 min, pumping off the hydrogen (0.06 mm) at −90°C, followed by warming the catalyst to room temperature or 100°C under further pumping. Catalysts prepared in this manner (Runs 5 and 7) are superior to those from previous activation procedures, since a twofold increase in activity is obtained while reproducibility approaches the accuracy of the deuterium determination (±2%). The improvement is even better when the catalyst is not heated to 100°C after activation. When the temperature of activation is lowered to −196°C, no activation of prereduced catalyst occurs (Run 6). If a catalyst, activated as above at −90°C, is further exposed to 1 atm of hydrogen for 12 min at 30°C, a decrease in activity and reproducibility is obtained (Run 8).

One final interesting observation concerning temperature of activation is the fact that *dry* platinum oxide ($PtO_2 \cdot 2H_2O$) does not reduce at −90°C even at a pressure of 1 atm of hydrogen, but does so explosively at a critical temperature of approximately −28°C.

Effect of Hydrogen Pressure and Rate of Hydrogen Addition

Up to this point in the investigation, all catalysts were activated at a hydrogen pressure of 1 atm, while 3 to 4 sec are usually necessary to fill the activation apparatus with this gas. It was therefore necessary to determine whether these two variables affect the activity and reproducibility of the catalyst. If the influence of hydrogen pressure is to be examined, the rate of hydrogen addition must be kept constant or made virtually instantaneous. This was achieved by including in the activation apparatus a large gas reservoir, which was isolated from the small catalyst chamber by a tap. The reservoir was filled with hydrogen to the required pressure and by quickly turning the tap, a reproducible, and instantaneous exposure to hydrogen was affected.

The results in Fig. 1 show that an increase of 400% in activity has occurred when a catalyst from the prereduced stock is activated at a pressure of 2 mm, instead of 760 mm, time and temperature of activation being kept constant at 12 min and −90°C. The graph reveals a surprising relationship between pressure and activity, in that the latter is seen to decrease sharply over the range 2–15 mm, and then to remain constant up to pressures of 80 mm. This plateau is followed by a further drop in activity, reminiscent of the critical pressure phenomenon in the $PtO_2 \cdot 2H_2O$ reduction, and a constant catalyst activity of 4.0% D hr^{-1} remains over the 100–760 mm pressure region.

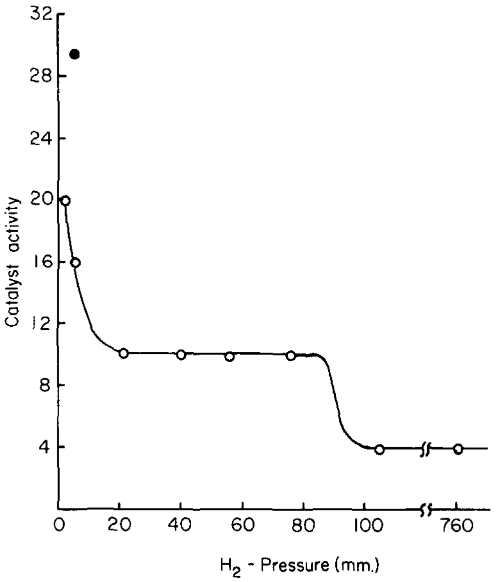

Fig. 1. Effect of hydrogen pressure and rate of hydrogen addition on catalyst activity (% D hr^{-1}). ○, Instantaneous hydrogen addition; ●, addition rate of 0.3 mm/sec.

Rate of hydrogen addition is also seen to affect catalyst activity since even in the low pressure activation region (5 mm), there appears to be an optimum rate of hydrogen addition. If the hydrogen is added over a period of 15 sec, a catalyst is obtained with a 67% higher activity than a control catalyst activated instantaneously at 5 mm. When the period of hydrogen addition is increased to 110 sec, catalyst activity is 39% lower than the control.

These results show that variations in pressure and hydrogen addition rate produce catalysts which may differ by as much as 600% in activity, but if these variables are strictly controlled and hydrogen addition made instantaneous then a catalyst possessing reasonable activity and a reproducibility of ±2% can be obtained.

Standard Activation Procedure

On the basis of the preceding work the following standard activation procedure (Procedure B) was adopted foı the exchange reactions. Prereduced catalyst stock from Procedure A in an ampoule containing a breakseal was evacuated at room temperature until all water vapor was removed; the catalyst (at −90°C) was then exposed to 1 atm of hydrogen by the instantaneous method for a period of 12 min, the hydrogen pumped off to 0.06 mm at −90°C, then the catalyst warmed to room temperature under further pumping to a pressure of 0.06 mm and vacuum-sealed.

Interaction between Catalyst and Reagent at Low Temperatures

In previous sections, catalyst reproducibility was considered from the viewpoint of activation procedures, the assumption being made that no changes occurred in the catalyst during the period of the exchange reaction as a result of an interaction with the organic substrate or heavy water. For this reason, reaction time in earlier experiments was kept constant, when comparisons of activity had been made within a given series. However, kinetic investigations of the benzene–deuterium oxide exchange reaction revealed that some catalysts yielded simple first order relationships whereas other catalysts prepared from stock which had been prereduced in a different manner exhibited significant deviations from unity, as typical graphs show in Fig. 2. This result could only be attributed to changes in the catalyst during the exchange reaction, hence catalyst reproducibility in this instance appears to be a function of both the activation procedure and catalytic deactivation occurring during reaction. These investigations were thus extended to determine the nature and cause of catalyst deactivation. Initial experiments were confined to exchange reactions occurring at temperatures of approximately 30°C.

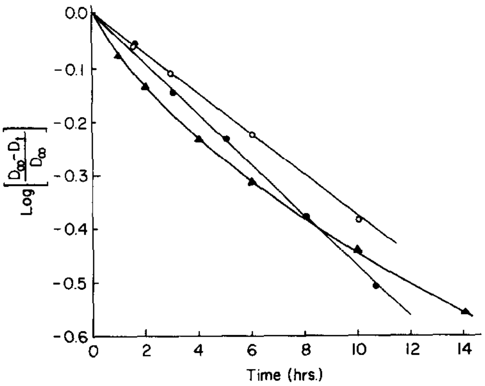

FIG. 2. Typical graphs for benzene–deuterium oxide exchange at 32°C. ●, ○, Catalysts stable to benzene; ▲, catalyst hypersensitive to benzene.

Catalyst Deactivation During Exchange

It is clear that the variables associated with catalyst deactivation originate in the prereduction procedure, since this is the one step which cannot be strictly controlled during catalyst preparation when the same stock of platinum oxide $PtO_2{\cdot}2H_2O$ catalyst and identical activation procedures are employed. It is then necessary to establish if deactivation of a hypersensitive catalyst, which occurs during the actual exchange reaction, is due to (*i*) thermal sintering (distinct from sintering occurring during catalytic activation, which has already been discussed), (*ii*) interaction between the catalyst and reactants (water and/or benzene), or (*iii*) a combination of both (*i*) and (*ii*).

In order to examine these three alternatives a modified reaction procedure was adopted whereby the catalyst, activated by Procedure B, was allowed to reside in contact with each of the reagents to be tested for a period of time before the actual exchange reaction was commenced. The time for exchange was sufficiently short so as to be negligible by comparison with the individual reagent residence time. From the results of these investigations (Fig. 3), it is evident that neither water nor thermal sintering is responsible for the observed severe catalyst deactivation, since both variables caused negligible decreases in activity even at 38.0°C. Benzene, however, causes a pronounced effect on catalyst activity; two types of benzene deactivation being revealed, depending on whether water is (a) present or (b) absent. In the former case (a), the instantaneous catalyst activity is calculated

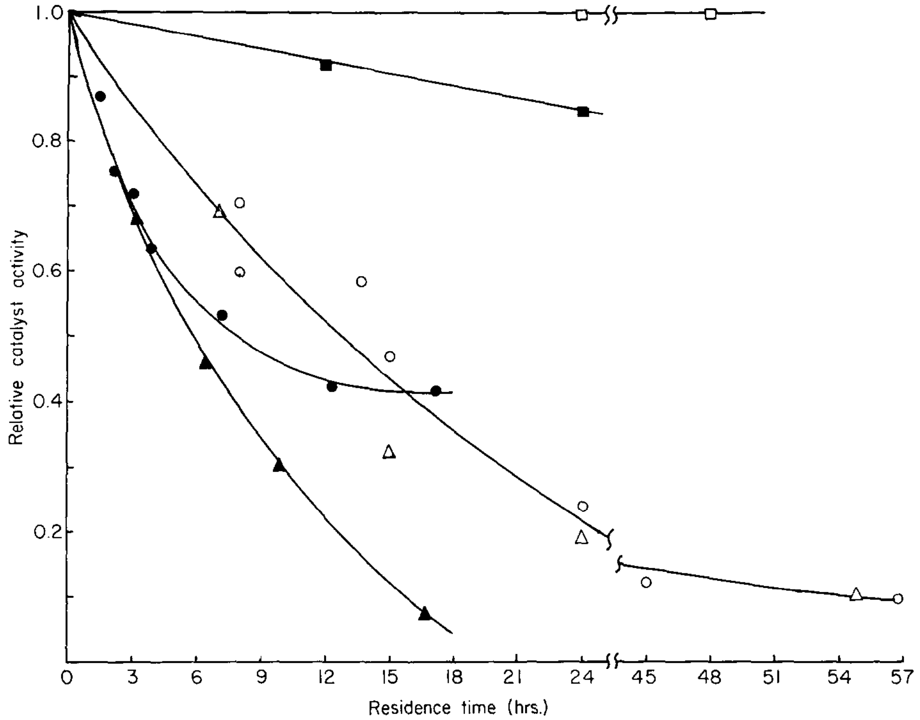

FIG. 3. Effect of reagent residence at low temperatures on the activity (k_T/k_0) of a hypersensitive catalyst. □, Catalysis in vacuum at 38.0°C; ■, D_2O at 38.0°C; ○, benzene at 32.0°C; ●, benzene and D_2O simultaneously at 32.0°C; △, 0.36 mole % anthracene in benzene at 32.0°C; ▲, 0.36 mole % anthracene in benzene and D_2O simultaneously at 32.0°C.

from tangents drawn to the curving kinetic graph in Fig. 2. The results (Fig. 3) are expressed as fractions of the initial catalytic activity remaining after a given time interval and they differ significantly from the results obtained for the corresponding graph involving benzene residence time [case (b)]. Deactivation of the exchange reaction occurs at an initially faster and more reproducible rate when both benzene and water are present than deactivation by benzene alone, the latter being characterized by a considerable scatter in results, plus a lower final activity of catalyst. Analogous results were obtained when the same prereduced catalyst, activated by procedure B, then thermal-sintered for 2 hr at 200°C, was exposed to benzene. In this instance, rate of decrease in catalyst activity was approximately the same as with the unsintered catalyst.

Effect of Other Organics

The deactivating effect of other organics such as anthracene, which is a known poison to exchange reactions (*3*), was compared with benzene by examining the relative reactivity of a benzene solution containing 0.36 mole % of this reagent (Fig. 3). As with pure benzene, two different deactivation processes were detected, depending on whether or not heavy water was present. The results also show that deactivation by the anthracene solution occurs in two stages. The initial rate of exchange, which is appreciably lower (50%) than that of pure benzene, suggests that reagent displacement is the main cause of poisoning. This stage in the poisoning action is followed by an interaction between the catalyst and the anthracene solution which eventually causes catalyst deactivation to occur at the same rate as with pure benzene and the final activities of the catalysts from the two systems are identical. Since the same stock of benzene containing a constant thiophene content (0.005%) was used in all reactions, the observed deactivation cannot be due to impurities.

Catalyst Sites

The alternate explanation remaining for the observed deactivation is that slight differences in the prereduction process produce a hypersensitive catalyst with differing active sites, some of which may be modified at 30°C by a specific interaction with benzene. It is noteworthy that, in a succeeding paper (Part VII), evidence will be presented to show that all catalysts may undergo similar changes *at high temperatures*. Modifications of different types may occur, from alterations in geometric and electronic factors to mere changes in the numbers of active sites. This may result in changes in activation energy of the reaction and/or cause displacement of one or another of the reagents from the catalyst surface. The problem may be clarified by measuring activation energies of exchange reactions on normal and deactivated hypersensitive catalysts.

Variation in Arrhenius Parameters with Catalyst Deactivation

For these experiments, catalyst deactivation was achieved by benzene exposure at 38.8°C using the technique described above. All relevant data is summarized in Table 2. Both normal and deactivated hypersensitive catalysts yield rate constants for the deuterium oxide–benzene exchange reaction which fit the conventional $\log_{10} k$/vs. $(1/T)$ plot, thereby confirming an Arrhenius-type relationship, i.e., $k = A \exp(-E/RT)$.

The results show that benzene deactivation at 38.8°C results in a doubling of the activation energy, however, this effect is largely compensated for by an increase in the frequency factor A and thus a plain sintering mechanism, i.e. decrease in the number of active sites, is eliminated. This result agrees with our previous data for the low deactivating effect of water. It would appear then that benzene is involved in a special interaction with the catalyst, in a manner which modifies existing sites, so that the reaction encounters a higher energy barrier. At the same time, benzene appears to generate new sites by a process which may well involve a π-complex type of interaction with the platinum surface (*2*, *3*, *8*).

Anderson and Kemball (*12*) have determined the activation energy and frequency factors for the exchange and hydrogenation reactions between benzene and deuterium gas on platinum. Their values show an interesting agreement with our results and seem to indicate a general inverse relationship between the number and activity of catalyst sites (*13*). With respect to absolute values of activation energies and catalyst activities, it is clear that these depend on both activation procedures and pretreatment of catalyst. Unless a strict control is maintained over these variables, considerable uncertainty must be attached to correlations between reaction rate constants and fundamental properties such as per cent *d* character of the different transition metal catalysts.

TABLE 2

VARIATION IN ARRHENIUS PARAMETERS WITH CATALYST DEACTIVATION

Catalyst residence under benzene at 38.8°C (hr)	Reaction temperature (°C)	Reaction time (hr)	% D in benzene	$k \times 10^4$ (% D sec^{-1})	E (kcal mole)	$\text{Log}_{10} A^a$	M
			Deactivated catalyst				
47.0	38.6	3.0	4.3	4.15			1.25
47.0	31.8	7.62	6.0	2.32	19 ± 1	29.1 ± 0.7	1.27
47.0	24.2	11.0	3.6	0.94			1.30
			Normal catalyst				
0	38.6	3.0	22.5	27.7			1.48
0	31.8	5.0	25.0	19.3	9.6 ± 0.5	23.6 ± 0.4	—
0	24.2	7.5	25.5	13.2			1.48

[a] A as molecules/sec/mg catalyst. Calculated from k', the rate constant expressed as number of deuterium atoms entering benzene per second per mg catalyst. Reagent/catalyst weight ratios are 48 and 63 for water and benzene, respectively.

Furthermore, our high values for the activation energies may be taken as further evidence that diffusion processes into the pores of the catalyst, or through the various liquid phases of the reagents, are not rate-determining, since such processes are characterized by activation energies in the order of 2–3 kcal/mole.

Deuterium Distributions in Labeled Benzenes

A representative number of deuterated benzenes from the exchange reactions described previously in this paper were examined by the technique of low voltage mass spectrometry in order to determine the possible mechanistic significance of the deuterium distribution in these labeled benzenes. Analyses were performed on a Metropolitan Vickers MS-2G mass spectrometer, correction being made for the natural abundance of heavy carbon and deuterium.

The technique was checked by comparing the experimentally determined deuterium distributions in a 50% deuterated and randomized benzene sample, to that calculated by Eq. (3). Satisfactory agreement between experimental and theory for the method was obtained. For random distribution in benzene, the mole fraction F_n of a species containing n deuterium atoms is given by the equation:

$$F_n = \frac{6!}{n!(6-n)!} X^n(1-X)^{(6-n)} \qquad (3)$$

where X is the fraction of hydrogen positions which on the average are occupied by deuterium atoms.

In general, poor agreement was observed between the experimentally determined deuterium distributions of benzene samples where the exchange reaction had not proceeded to completion and those calculated by Eq. (3). The fact that deuterium was incorporated into benzene in a nonrandom manner suggests that Anderson and Kemball's (*12*) theory of multiple and stepwise exchange also applies to the benzene-heavy water system. These authors derived kinetic expressions which give a measure of the relative importance of each type of mechanism.

The first of these equations was used to calculate the rate of entry of deuterium into benzene

$$-\log_{10}(\phi_\infty - \phi) = (k_\phi t/2.3\phi_\infty) - \log \phi_\infty \qquad (4)$$

where k_ϕ is the initial rate of entry of deuterium atoms into 100 molecules of d_0-benzene per unit time. ϕ is defined by the equation

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

where u to z represent the percentages of total benzene present as d_1 to d_6-benzene and ϕ_∞ is the equilibrium value.

The second rate considered was the disappearance of d_0-benzene which was given by:

$$-\log_{10}(b - b_\infty) = [k_b t/2.3(100 - b_\infty)] - \log(100 - b_\infty) \qquad (6)$$

where k_b is the initial rate of disappearance of d_0-benzene, b is the percentage of benzene present at time t as d_0-benzene and b_∞ is the equilibrium value.

The mean number of deuterium atoms reacting per benzene molecule is then given by Eq. (7). It should be noted that

$$M = k_\phi/k_b \qquad (7)$$

If only stepwise exchange occurs, M has a value of unity and the deuterium distribution is given by Eq. (3).

The results of the various M value calculations are summarized in Tables 2 and 3 for benzene exchange on catalysts prepared by different procedures. The marked deviation of M values from unity suggests that the catalytic deuteration of benzene by heavy water occurs by both stepwise and multiple-dissociative exchange mechanisms. The values of M are generally of the same order of magnitude as those reported by Anderson and Kemball for deuterium–benzene exchange on platinum (*12*). It thus appears that aromatic hydrocarbons exchange with heavy water by predominantly the same mechanism as aliphatic hydrocarbons, i.e. only C–H bond rupture occurs while π-electron delocalization is maintained. The fact that aromatic molecules experience C–H bond rupture more readily

TABLE 3

VARIATION IN DEUTERIUM DISTRIBUTION IN BENZENE WITH CATALYST ACTIVATION

Activation procedure		Percentage composition[a]								
Hydrogen pressure (mm)	Time of hydrogen addition (sec)	C_6H_6	C_6H_5D	$C_6H_4D_2$	$C_6H_3D_3$	$C_6H_2D_4$	C_6HD_5	C_6D_6	k_ϕ	M
760	Instantaneous	79.6	12.7	4.43	1.86	.79	.38	.20	23.6	1.55
760	Instantaneous	20.7	30.4	24.4	14.9	6.70	2.37	.54	24.1	1.50
39	Instantaneous	62.4	16.5	8.60	5.49	3.64	2.36	1.17	65.1	2.07
21	Instantaneous	61.6	15.3	9.30	6.02	4.05	2.47	1.14	68.7	2.02
5	Instantaneous	47.1	23.9	12.8	7.62	4.92	2.72	.98	92.8	1.84
2	Instantaneous	44.4	19.8	13.9	10.1	6.82	3.74	1.37	104.3	1.91
5	10	15.3	31.0	29.4	16.5	6.3	1.58	.08	171.6	1.33
5	15	26.5	32.4	22.0	11.5	5.37	1.92	.34	130.6	1.44

[a] Equilibrium deuterium content = 50%.

than aliphatics (i.e. faster exchange when reagent displacement doesn't occur) is attributed to π-complex interaction with the catalyst surface which lowers the activation energy in the actual C–H bond rupture process (*2*, *3*, *9*).

A further significant feature of these results is the variation in the *M* factor with catalyst pretreatment (Table 2) and different activation procedures (Table 3). When the catalyst is activated at different hydrogen pressures, *M* does not increase with increasing catalyst activity but reaches a maximum value in the 15–80 mm pressure range. In general, different hydrogen activation procedures yield catalysts of different activities with their own characteristic *M* values. However, since stepwise and multiple exchange reactions presumably occur on different sites, the different activation procedures not only affect the number and activity, but also the nature or pattern of the active sites.

Deactivation of the catalyst with benzene invariably decreases the *M* value.* This, however, does not mean that active centers on which multiple exchange occurs are more vulnerable, but rather that the deactivation process, which actually is a process whereby new catalyst sites are generated ($\log_{10} A$ increases from 23.6 to 29.1), favors the creation of sites for stepwise exchange.

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* It will be shown in Part VII of this series (*9*) that high temperature deactivation has the same effect.