Deuterium and Tritium Labelling of Aromatic Hydrocarbons by Zeolite-catalysed Exchange with Perdeuteriobenzene, Tritiated Benzene, and [p-^{3}H]Toluene

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Three hydrogen zeolites, HNaY, H-Mordenite, and HZSM-5, have been employed as catalysts for hydrogen isotope exchange reactions. The zeolites catalysed exchange between the isotope sources perdeuteriobenzene, tritiated benzene, and [p-^{3}H]toluene, and a wide range of organic substrates, thus providing a useful labelling technique. The extent and orientation of exchange in reaction products were assessed through the techniques of radio-gas chromatography, mass spectrometry, and ^{3}H n.m.r. spectroscopy. Substituted benzenoid compounds were non-specifically labelled in the aromatic centres at temperatures from 40 to 175 °C, but heterocyclic compounds and alkanes were not exchanged. A series of competitive exchange experiments gave an insight into the reasons for the lack of reactivity of some substrates. Inspection of the multiple exchange parameters and relative rates of exchange of substrates of different bulk suggested correlations between zeolite pore sizes, substrate reactivity, and labelling patterns. Consideration of these experimental results together with those from redistribution reactions with [p-^{3}H]toluene led to interpretation of results in terms of acid exchange mechanisms, where these mechanisms are mediated by the constraints of zeolite pore geometry.

The use of zeolites as catalysts for labelling compounds with deuterium or tritium has been reported recently.[1–3] Both tritiated water and tritium gas have been proposed as isotope source.[2,3] In the latter case it was necessary to include a noble metal such as platinum with the zeolite to promote efficient activation of elemental tritium or a non-aromatic substrate such as cyclohexane. In the absence of a metal component in the catalyst the exchange pattern observed in aromatic compounds was typical of electophilic substitution, namely *ortho–para* in molecules such as alkylbenzenes and halogenobenzenes. The inclusion of a metal such as platinum or palladium introduced some metal character into the exchange pattern, and thus in alkylbenzenes some alkyl exchange was observed, and the *meta*-position of the ring was likewise activated.

The technique of using small quantities of tritiated water as isotope source with the zeolite is not generally applicable to deuterium labelling since the quantities of D_2O necessary to yield substantial deuterium abundance in the substrate would deactivate the zeolite. Hence it has been observed[4] that temperatures of 300 °C are necessary to induce appreciable exchange between D_2O and benzene over NiX zeolite. At these substantially increased temperatures hydrocarbons would be susceptible to a range of isomerisation and conversion reactions.

We have now explored the use of a third common isotope source for hydrogen isotope labelling, namely perdeuteriobenzene, in the zeolite-catalysed exchange system. Other organic isotope sources such as tritiated benzene and [p-^{3}H]toluene have also been investigated, and are reported here. These tritium- and deuterium-containing organic isotope sources have the advantage over elemental tritium or deuterium that gas handling equipment is not necessary. Furthermore, they are applicable to catalyst systems such as the zeolites Y, Mordenite, and ZSM-5 which are deactivated by substantial quantities of water.

Experimental

The organic substrate (0.1 ml, or 0.1 g for solids) was placed in a reaction tube along with zeolite catalyst (*ca.* 25 mg) and isotope source (0.1 ml). The reaction ampoule was flame-sealed at atmospheric pressure, and heated to the required temperature in an oven in a well ventilated fumehood. In competitive exchange experiments toluene (0.05 ml) and a second substrate (0.05 ml) were reacted with the usual quantities of catalyst and isotope source.

Tritiated samples were analysed for purity and total activity by radio-g.l.c.,[5] and for orientation of exchange by ^{3}H n.m.r., as described elsewhere.[2,6] ^{3}H N.m.r. assignments were deduced from a consideration of the spectra of compounds labelled by a variety of exchange and synthetic procedures. Deuteriated samples were analysed by low-voltage mass spectrometry (10—15 eV), and corrected for naturally occurring isotopes. % D values were calculated with only exchangeable hydrogens being considered (*e.g.* five in toluene). % Incorporation values, representing the observed % D as a percentage of the projected % D value after infinite time, were also derived. The term % Approach to Equilibrium is not used in this context, as the observation of a random distribution of isotope between substrates is not necessarily coincident with a random distribution within the substrates.

Values of the multiple exchange parameter, M,[7] were determined for samples containing $<20\%$ deuterium, by the formula previously published.[8]

HNaY zeolite was prepared from Linde SK-40 by exchange with NH_4NO_3 to 3% residual Na and activation to 400 °C under nitrogen. H-Mordenite and HZSM-5 were prepared by acid exchange with HCl (0.3M). H-Mordenite was activated at 420 °C, while HZSM-5 was calcined at 500 °C.

Results and Discussion

Exchange with C_6D_6.—Perdeuteriobenzene was exchanged with a variety of aromatic compounds over the hydrogen forms of three zeolites commonly used to catalyse hydrocarbon conversion reactions, *i.e.* Y-zeolite, Mordenite, and ZSM-5. Table 1 lists the results of these reactions. Exchange was observed at temperatures as low as 40 °C, and for most aromatic hydrocarbons was relatively fast at 125 °C. These temperatures are well below the onset of zeolite-catalysed hydrocarbon conversion reactions and the procedure thus represents a satisfactory and clean labelling method.

Halogenobenzenes exhibit somewhat slower exchange rates than alkylbenzenes under equivalent conditions, and fluorobenzene is the most rapidly labelled. The slow exchange of

Table 1. Zeolite-catalysed exchange of substituted aromatic compounds with C_6D_6

Compound[a]	Zeolite	Time (h)	Temp. (°C)	% D[b]	% Incorporation	*M* Value
Toluene	HNaY	44	100	32.0	54.0	
Isopropylbenzene	HNaY	215	125	28.0[c]	61.1	
Naphthalene	HNaY	18	100	46.5	89.4	
Triphenylmethane	HNaY	168	175	18.0	25.0	
Toluene	H-Mordenite	238	40	19.9	33.7	1.0
Toluene	H-Mordenite	24	100	28.1	47.6	
Isopropylbenzene	H-Mordenite	24	100	1.8[c]	3.9	1.0
t-Butylbenzene	H-Mordenite	24	100	3.7[c]	8.7	1.1
t-Butylbenzene	H-Mordenite	96	125	28.5[c]	66.4	
Naphthalene	H-Mordenite	24	100	1.5	3.0	1.0
o-Xylene	H-Mordenite	24	100	15.9	23.9	1.1
p-Xylene	H-Mordenite	24	100	11.8	17.4	1.0
Hemimellitene	H-Mordenite	192	125	6.7	8.9	1.1
Mesitylene	H-Mordenite	192	125	55.1	72.7	
Fluorobenzene	H-Mordenite	72	125	8.5	15.1	1.0
Chlorobenzene	H-Mordenite	72	125	2.3	4.0	1.0
Bromobenzene	H-Mordenite	72	125	1.2	2.1	1.3
Anisole	H-Mordenite	24	100	7.4	12.5	1.0
Toluene	HZSM-5	24	40	8.1	13.8	1.1
Toluene	HZSM-5	48	125	23.4	39.7	
Isopropylbenzene	HZSM-5	24	125	19.1	29.2	1.5
t-Butylbenzene	HZSM-5	120	125	5.0	7.4	1.3
Naphthalene	HZSM-5	24	125	7.8	14.9	2.3
o-Xylene	HZSM-5	8	125	3.4	5.2	2.0
p-Xylene	HZSM-5	4	125	2.6	3.9	1.1
Hemimellitene	HZSM-5	192	125	<1	<1	
Mesitylene	HZSM-5	192	125	2.1	2.8	1.3
Fluorobenzene	HZSM-5	24	125	4.7	8.4	1.0
Chlorobenzene	HZSM-5	24	125	2.4	4.2	1.0
Bromobenzene	HZSM-5	24	125	3.2	5.5	
Anisole	HZSM-5	24	125	2.7	4.5	1.0

[a] Cyclohexane, n-hexane, 2,3-dimethylbutane, furan, pyrrole, pyridine, and nitrobenzene all showed negligible exchange after 100 h at 125 °C over HZSM-5 and H-Mordenite. [b] Calculated assuming all aromatic hydrogens exchangeable in all substrates. [c] Calculated assuming methyl hydrogens also exchangeable.

halogenobenzenes was also noted in exchange reactions with HTO over HNaY zeolite, and was thought to reflect the deactivation of these substrates towards electrophilic aromatic substitution.[2] Larger molecules such as t-butylbenzene and naphthalene exchange at somewhat slower rates than other n-alkyl aromatic compounds, particularly on the small-pore ZSM-5 zeolite, and this probably reflects the constraints imposed on the movement of the molecule through the zeolite pore structure. Hemimellitene exhibits slow exchange on Mordenite and is inactive on ZSM-5. Typical dimensions for the larger pores of the zeolites are: Y-zeolite, 0.74—0.80 nm; Mordenite, 0.58—0.69 nm; ZSM-5, 0.52—0.56 nm.

The proposal that the movement of molecules is restricted in the small-pore zeolites is supported by the observation of multiple exchange parameters (*M* values) substantially greater than unity early in the exchange cycle for these large molecules. Hence, while *o*-xylene exhibits an *M* value close to 2 on ZSM-5, the *M* value for *p*-xylene exchange is close to unity. Thus it seems the movement of *o*-xylene through the pore system of ZSM-5 is hindered relative to that of *p*-xylene, as has been previously noted.[9]

In exchange studies of hydrocarbons over metal surfaces the observation of *M* values greater than unity is interpreted as indicating association of the exchanging molecules with the catalytic site for a period of time sufficiently long that more than one atom may exchange per residence on the catalytic site. In analogy with this interpretation it is thought likely that the multiple exchange observed with the current zeolite systems reflects a residence for the molecules within the zeolite pore structure for a period long enough to allow exchange of several atoms within the substrate before its diffusion from the pore into the bulk liquid phase. Hence it is possible to categorise the molecules showing slow exchange on ZSM-5 into those constrained in their activity by virtue of their size (such as t-butylbenzene and hemimellitene), and those deactivated by normal electronic effects (such as the halogenobenzenes).

Neither alkanes nor a number of heterocycles exhibited detectable exchange with C_6D_6 (Table 1, footnote). Alkanes have previously been shown to be inactive towards exchange with traces of tritiated water up to 175 °C.[2] In contrast the heterocycles furan and pyrrole were previously shown to label readily in exchange with HTO under conditions which favoured aromatic exchange on HNaY zeolite.[2] A contrasting result between C_6D_6 exchange and HTO exchange was also observed in studies of Lewis acid catalyst systems.[10] The result was interpreted as indicating a 'poisoning' of the catalytic system by the heterocycle, as competitive studies with toluene confirmed.

Some typical mass spectral distribution patterns for a number of compounds selected when at least 20—30% deuterium had entered are contained in Table 2. At this particular stage of the exchange cycle the number of active positions in the molecule is apparent. For toluene and other non-branched alkylbenzenes molecules containing up to five deuteriums (*i.e.* D_5) only were observed, indicating that exchange was likely to be confined to aromatic hydrogen atoms. In agreement with this, naphthalene showed exchange at all eight positions. In contrast some branched alkyl aromatic compounds, such as isopropylbenzene and s-butylbenzene,

Table 2. Typical mass spectral distribution patterns following exchange with C_6D_6

Compound	Zeolite	Deuterium distribution D_0	D_1	D_2	D_3	D_4	D_5	D_6	D_7	D_8	% D
Toluene	HNaY	15.4	33.7	31.8	15.1	3.7	0.4				31.9
Toluene	H-Mordenite	18.2	38.4	30.3	11.2	1.8	0.1				28.1
Toluene	HZSM-5	17.0	36.0	30.0	13.0	3.0	0.3				30.0
Naphthalene	HNaY	0.7	4.8	14.2	24.7	26.6	18.5	8.2	2.1	0.2	46.5
Naphthalene	HZSM-5	29.0	27.0	18.0	12.0	7.3	4.1	1.9	0.6	0.2	21.0
Isopropylbenzene	HNaY	3.3	10.9	20.8	26.4	22.3	12.2	4.4	0.3		28.2
Isopropylbenzene	HZSM-5	47.4	25.8	15.2	8.0	2.9	0.7				19.1
n-Butylbenzene	H-Mordenite	1.2	10.3	27.1	33.8	21.6	6.0				56.5
Isobutylbenzene	H-Mordenite	2.2	5.8	17.1	32.2	30.8	12.0				64.0
s-Butylbenzene	HNaY	10.4	22.2	24.4	17.4	9.2	3.2	14.3	0.0	0.2	26.3
s-Butylbenzene	H-Mordenite	0.7	5.0	18.6	33.7	30.8	11.3				64.6

Table 3. Exchange with C_6H_5T over HNaY and HZSM-5 zeolites

Compound	Zeolite	Time (h)	Temp. (°C)	% Incorporation	% Distribution per H	
Toluene	HNaY	24	100	58	*ortho*	18.0
					meta	20.0
					para	24.0
					Methyl	<1
Toluene	HZSM-5	117	125	76	*ortho*	29.0
					meta	11.0
					para	21.0
					Methyl	<1
Isopropylbenzene	HNaY	235	125	40	Aromatic	N.a.[a]
					Methine	<1
					Methyl	17.0
Isobutylbenzene	HNaY	235	125	53	*ortho*	25.0
					meta	17.0
					para	17.0
					Alkyl	<1
s-Butylbenzene	HNaY	144	175	76	Aromatic	N.a.[a]
					Methine	<1
					Methylene	17.0
					β-Methyl	22.0
					γ-Methyl	<1
t-Butylbenzene	HNaY	144	175	74	*ortho*	8.4
					meta	8.0
					para	10.0
					Methyl	6.3
Naphthalene	HNaY	168	175	51	α	10.0
					β	15.0
Naphthalene	HZSM-5	117	125	74	α	14.0
					β	11.0
Pyrene	HNaY	168	175	18		
Pyrene	HZSM-5	117	125	<1		
Bromobenzene	HNaY	24	195	82	*ortho*	24.0
					meta	8.0
					para	36.0
Furan	HNaY	235	125	<1		
Thiophene	HNaY	168	175	<1		

[a] N.a. = Contribution to orientation not assessed.

showed exchange beyond D_5 over HNaY zeolite, while isobutylbenzene exhibited exchange in five positions only. In previous studies of exchange with tritiated water over HNaY zeolite it was shown that alkyl exchange was confined to the β-carbons of alkylbenzene molecules branched at the α-carbon.[2] The current deuterium results support a similar conclusion. However, no evidence for alkyl labelling in several alkylbenzenes was detected for C_6D_6 exchange over HZSM-5 catalyst, and this is supported by extensive investigations using HTO as isotope source.[11]

Exchange with Tritiated Benzene.—In order to confirm the suspected deuterium isotope orientation patterns a series of exchange experiments were performed with tritiated benzene as isotope source and samples were analysed by ^3H n.m.r. spectroscopy (Table 3). These results for alkylbenzenes do indeed confirm that exchange in alkyl substituents occurs only over HNaY, and in isolated cases over H-Mordenite, where the molecule is branched at the α-carbon. Furthermore the alkyl tritium appears only in positions β to the aromatic nucleus. This exchange pattern thus parallels closely that of tritiated water

Table 4. Redistribution of isotope within [p-^{3}H]toluene, and exchange with benzene over zeolite catalysts

		Time	Temp.	% Distribution per H				
Reactants	Zeolite	(h)	(°C)	*o*	*m*	*p*	CH_3	Benzene
Toluene		0		< 1	< 1	100.0	< 1	
Toluene	HNaY	81	125	25.0	11.0	24.0	< 1	
Toluene–benzene	HNaY	81	125	15.0	13.0	22.0	< 1	3.7
Toluene	H-Mordenite	24	125	6.0	1.7	84.5	< 1	
Toluene	H-Mordenite	96	125	19.8	18.0	24.5	< 1	
Toluene–benzene	H-Mordenite	24	125	22.3	5.1	24.5	< 1	3.4
Toluene–benzene	H-Mordenite	96	125	7.8	7.2	8.5	< 1	10.2
Toluene	HZSM-5	24	125	5.8	2.8	82.8	< 1	
Toluene–benzene	HZSM-5	24	125	11.2	2.9	65.0	< 1	1.1

Table 5. Toluene competition experiments with C_6D_6, catalysed by H-Mordenite and HZSM-5[a]

Compound[b]	Zeolite	No. of exchangeable hydrogens	% D	Incorporation	*M* Value
Toluene	H-Mordenite	5	< 1	< 1	
Furan		4	2.4	4.2	
Toluene	H-Mordenite	5	36.2	61.9	
Nitrobenzene		5	< 1	< 1	
Toluene	H-Mordenite	5	19.2	32.3	1.0
Anisole		5	19.4	32.8	1.0
Toluene	HZSM-5	5	2.1	3.7	2.9
Thiophene		4	< 1	< 1	
Toluene	HZSM-5	5	30.5	52.0	
Nitrobenzene		5	< 1	< 1	
Toluene	HZSM-5	5	6.6	11.2	1.0
Anisole		5	8.0	13.5	1.0

[a] Reaction time 24 h. [b] Toluene was also reacted in the presence of thiophene, pyrrole, aniline, and pyridine over H-Mordenite zeolite, and no exchange was detected in either substrate. Similarly, toluene was reacted in the presence of pyrrole, furan, aniline, and pyridine over HZSM-5, and no exchange was detected in either substrate.

exchange.[2,11] However, in marked contrast to the earlier water exchange results, exchange within the aromatic nucleus of alkylbenzenes shows considerable activity within the *meta* positions, there being little evidence for the marked *ortho–para* preference typical of electrophilic substitution. Likewise, in naphthalene exchange occurs readily in both α- and β-positions, in contrast to the water exchange results. Only in the slower exchanging halogenoaromatics was there a significant orientation in favour of *ortho-* and *para-*positions.

Exchange of [p-^{3}H]*Toluene*.—In order to investigate in more detail the relative reactivity of hydrogen atoms in the toluene–benzene system, a sample of specifically labelled [p-^{3}H]toluene was prepared [12] and allowed to exchange over the zeolites, both in the presence and absence of non-labelled benzene. The results reported in Table 4 show that the redistribution of tritium from the *para*-position in [p-^{3}H]toluene occurs with a significant preference for *ortho-* and *para*-positions such that, at a point in time where the isotope is randomly distributed between *ortho-* and *para*-positions, the *meta*-position is well below an equilibrium value (*i.e.* 20%). In the presence of benzene the rate of entry of isotope into benzene is considerably lower than the rate of redistribution of isotope within toluene itself (*e.g.* the H-Mordenite and HZSM-5 results after 24 h). Hence, the rate of exchange of a single benzene position is slower than the slowest aromatic position in toluene. It thus appears that the absence of a labelling pattern typical of electrophilic exchange in the C_6D_6 and C_6H_5T exchange systems reported in Tables 1 and 3 may be explained on the basis that a redistribution of isotope occurs within the labelled substrate at a rate faster than the incorporation of isotope from benzene itself. Even early in the exchange cycle of most molecules the preference for exchange at the *ortho-* and *para*-positions is obscured by the concomitant isotope redistribution reaction.

The fact that a significant isotope distribution was observed in bromobenzene (Table 3) suggests that this molecule is sufficiently deactivated by the halogeno-substituent that its inherent rate of exchange approaches or is lower than that of benzene itself. It has previously been shown [2] that the rates of exchange of benzene and bromobenzene with HTO are comparable.

Competition of Substrates with Toluene in C_6D_6 *Exchange*.—A series of compounds were reacted with C_6D_6 in the presence of toluene over H-Mordenite and HZSM-5 catalysts. The time and temperature of exchange were chosen such that toluene would have exchanged close to 100% incorporation with C_6D_6 in the absence of a further substrate.

The experiments were performed to differentiate between circumstances where exchange of a substrate was prevented by its poisoning of the catalyst to the exclusion of benzene and those where its own inactivity led to no exchange with the C_6D_6. The results of a selection of the reactions performed are listed in Table 5.

It may be noted from Table 5 that most of the substrates were not labelled, and also that toluene was not labelled in the presence of many of them. The results may be interpreted in terms of competitive adsorption on the catalyst where the isotope source is one of the less efficient competitors, and so few of the substrates were labelled.

As no deuterium was lost from the C_6D_6 during reaction it is probable that pyrrole, aniline, and pyridine all totally prevented the benzene from exchange with the surface, and probably also totally excluded toluene. The fact that toluene exchanged in the presence of nitrobenzene suggests that the lack of exchange in nitrobenzene is a consequence of its deactivating substituent, and not because of participation in poisoning reactions on the catalyst surface.

Toluene and anisole were labelled at approximately the same rate by C_6D_6, and both were labelled in a stepwise manner. This suggests that they have very similar adsorption properties within the zeolites, and compete very equally for deuterium.

Mechanism of Exchange.—The pre-treatment of the zeolites and their use under anhydrous conditions provides for the presence of some Lewis acid sites as well as Brönsted sites on the zeolite surface. The addition of many of the aromatic reagents leads to marked colouration of the zeolite suspension, suggesting the presence of charge-transfer-type complexation such as in the Lewis acid hydrogen isotope exchange procedures. Considerable e.s.r.[13] and i.r.[14] evidence also exists for the formation of charge-transfer complexes of benzene and other aromatics with zeolites in the absence of water. Previous workers have proposed that exchange occurs by incorporation of isotope into the residual Brönsted acid sites on the zeolite followed by exchange into the organic molecule.[15] An electrophilic substitution mechanism by a Brönsted acid appears to satisfy the exchange patterns observed within the aromatic nuclei. It is conceivable that this may occur preferentially while the aromatic species is bound at a Lewis acid site, which provides for exchange at temperatures as low as 40 °C. The addition of water to the zeolite leads to the conversion of any Lewis sites to Brönsted sites and deactivates the catalyst and temperatures as high as 180 °C are then required to promote exchange on HNaY zeolite.

The observation that alkyl exchange occurs only in molecules branched at the α-carbon supports the view that the mechanism involves hydride transfer between a reactant molecule and an α-carbonium ion as described elsewhere.[16,17] Incorporation of isotope into the carbonium ion may take place by deprotonation to an olefinic intermediate and reprotonation,[17,18] or by direct exchange of the carbonium ion. The reduced level of alkyl exchange over H-Mordenite, and the complete absence of any alkyl labelling over HZSM-5 catalyst, are thought to reflect the constraints imposed on the formation of intermediates by the pore size of the zeolites. Hence as the pore sizes decrease, the formation of the intermediate in alkyl exchange becomes increasingly difficult, until it is completely disfavoured over HZSM-5.

Conclusions.—As a method of producing either deuterium- or tritium-labelled compounds this procedure involving exchange with benzene as isotope source usefully complements the Lewis acid labelling procedures, where catalysts such as ethylaluminium chloride were used with perdeuteriobenzene, and metal-catalysed exchange procedures. The complication of intramolecular substituent shifts as observed in the Lewis acid labelling of disubstituted aromatics[19] appears to be absent from the zeolite procedure. Biphenyl formation does not accompany benzene exchange, in contrast to some noble metal exchange procedures.[20] The technique is applicable to deuterium as well as tritium, unlike the water–zeolite labelling system previously proposed,[2] where the quantities of D_2O necessary to yield adequate isotope concentrations would vastly decrease the activity of the catalyst at modest temperatures. The procedure represents an efficient one-step method for producing aromatic molecules generally labelled in the aromatic centre.

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