Rhodium Trichloride as a Homogeneous Catalyst for Isotopic Hydrogen Exchange. Comparison with Heterogeneous Rhodium in the Deuteriation of Aromatic Compounds and Alkanes

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Summary The use of rhodium trichloride as a homogeneous catalyst for the exchange of aromatic compounds and alkanes is described; comparison of the results with corresponding data from heterogeneous rhodium metal and other homogeneous systems, *e.g.*, platinum and iridium, supports the proposal that specific types of π-complex mechanisms are common to all such exchange systems.

EXTENSIVE data have been published for the isotope exchange of organic compounds with D_2O in the presence of homogeneous $PtCl_4^{2-}$ and heterogeneous platinum[1,2] and to a lesser extent for the analogous homogeneous and heterogeneous iridium systems.[3] We now report, for the first time, the use of $RhCl_3$ as a homogeneous catalyst for the same deuterium exchange reactions involving both aromatic compounds and alkanes (Tables 1 and 2). In addition, we include further heterogeneous rhodium data as previously published results[4] did not include the necessary relevant compounds required for the present comparison purposes.

The exchange results with $RhCl_3$ as a homogeneous catalyst show a number of significant features. (i) This catalyst is thermally more stable than $PtCl_4^{2-}$, but less stable than iridium. (ii) Exchange is slower than with either platinum or iridium, occurs with a high M value (typically 3·7 for benzene), and leads to appreciable deuteriation of both aromatic ring and side chain in the alkylbenzenes. (iii) Orientation of isotope in the side chain of the long chain alkylbenzenes (*e.g.*, n-butylbenzene) is analogous to that found with platinum and iridium and suggests the participation of a similar type of mechanism, *i.e.*, the terminal abstraction π-complex (TAPC) process. (iv) As with the platinum and iridium systems, *ortho* steric effects are observed in alkylbenzene exchange. (v) Rhodium is less active than platinum in promoting halogenobenzene exchange (Table 2) and the halogenobenzenes exchange slower than the alkylbenzenes, while the effect of the substituent (in the order F>Cl>Br>I) remains as in the platinum system. (vi) Excess of mineral acid is not required to stabilise the catalyst solution in contrast to the $PtCl_4^{2-}$ system as excess of acid retards the rhodium catalyst exchange rate. (vii) Finally, rhodium catalyses exchange in saturated hydrocarbons as typified by cyclohexane (Table 2), although deuteriation of this compound is very much slower than benzene. Inclusion of a polycyclic aromatic compound, such as pyrene, enhances cyclohexane exchange as with platinum.[2]

Both homogeneous and heterogeneous rhodium catalyse exchange in the side chains as well as the rings of the alkylbenzenes. With heterogeneous rhodium, deuteriation in the side chain of the long chain derivatives, such as n-butyl benzene, decreases along the chain away from the ring in a manner analogous to that observed for platinum.[2] It is thus likely that the mechanism of exchange, as with heterogeneous platinum, involves an initial π-complex to the metal through the ring followed by an α–β migration to the terminal position.[2]

Nitrobenzene exchange is completely self-poisoned with heterogeneous rhodium but not with homogeneous rhodium, and as such serves as an ideal compound for distinguishing between heterogeneous and homogeneous processes as with platinum and iridium systems.

An important feature of the heterogeneous rhodium results is the remarkable degree of poisoning of the catalyst by all halogenobenzenes in contrast to their reactivity with platinum.[2] Slight poisoning is also observed in the case of homogeneous rhodium. The fact that fluorobenzene, in competitive heterogeneous studies with benzene, completely poisons benzene exchange but is not deuteriated readily itself, suggests that the toxicity phenomenon involves an effect stronger than poisoning *via* simple charge-transfer bonding through the halogen.[2] A more plausible suggestion involves dehalogenation[6] with the formation of the corresponding hydrogen halide which is particularly toxic to heterogeneous rhodium catalysts.[7] In this respect it is significant that even when borohydride-reduced $RhCl_3$ is replaced with hydrogen-reduced Rh_2O_3 as catalyst, the poisoning of the halogenobenzenes heterogeneously is still severe.

TABLE 1. Deuterium exchange in alkylbenzenes with homogeneous and heterogeneous rhodium

	C_6H_6	PhMe	o-MeC_6H_4Me	p-MeC_6H_4Me	$PhBu^n$	$PhBu^t$
Homogeneous atom %D	17·7[a]	15·0[b]	13·0[b]	2·0[b]	5·4[c]	7·6[c]
%D in ring	17·7	18·0	21·2	—	12·0	16·0
,, α-CH_2					5·0	
,, other CH_2					0·0	
,, Me		10·0	7·3	—	1·7	2·9
Heterogeneous atom %D	26·5[d]	42·0[d]	25·8[d]	22·8[d]	7·7[e]	17·4[d]
%D in ring	26·5	36·6	14·0	0·8	6·3	41·8
,, α-CH_2					11·2	
,, other CH_2					9·3	
,, Me		50·8	33·0	37·0	5·5	3·8

[a] Homogeneous exchange conditions: $RhCl_3.3H_2O$ (0·02 M) in $MeCO_2D$–D_2O (1 : 1) for 96 h at 130 °C; theoretical extent of deuteriation (assuming equilibration of all H in the system) 50%. Blanks without rhodium salt gave no exchange. Deuterium analysis was by n.m.r. and mass spectrometry.[2] [b] Same as [a] except 130 h. [c] Same as [b] except $RhCl_3.3H_2O$ (0·1 M). [d] Heterogeneous exchange conditions: $RhCl_3.3H_2O$ reduced with aqueous $NaBH_4$;[2] exchange with D_2O for 46 h at 130 °C except benzene (24 h), D (theor.) 50%. [e] Same as [d] except 72 h at 150 °C; D (theor.) 80%.

TABLE 2. Deuterium exchange in halogenated benzenes, nitrobenzene, and cyclohexane with homogeneous and heterogeneous rhodium

			Deuterium distribution					
Compound	Catalytic system	Atom %D	D_0	D_1	D_2	D_3	D_4	D_5
PhF	Homo[a,b]	9·8	71·4	17·5	5·7	2·9	1·8	0·7
,,	Het[c,d]	0·9	96·2	3·1	0·7			
PhCl	Homo[a]	7·7	76·6	15·0	5·0	3·4	0·6	0·1
,,	Het[c]	0·3	98·9	0·9	0·3			
PhBr	Homo[a]	5·8	81·3	12·4	3·7	1·5	0·4	0·4
,,	Het[c]	0·2	99·1	0·8	0·1			
PhI	Homo[a]	0·0	100·0					
$PhNO_2$	Homo[a]	3·4	87·9	9·4	1·9	0·4	0·4	0·2
,,	Het[c]	0·0	100·0					
C_6H_{12}	Homo[a]	0·1	99·2	0·7	0·1			
,,	Homo[a,e]	0·15	98·6	1·2	0·2			

[a] Same conditions and analyses as in footnote[a] of Table 1, except for a 200 h reaction time. [b] Same as [a] except $RhCl_3.3H_2O$ 0·1 M 14·4 atom %D incorporated after 96 h. [c] Heterogeneous exchange conditions: $RhCl_3.3H_2O$ reduced with $NaBH_4$,[2] reaction for 46 h at 130 °C, D (theor.) 50%. [d] In competing exchange of C_6H_6 and PhF under conditions[c] benzene almost completely poisoned. [e] With pyrene added: [pyrene] = [cyclohexane] = $9·3 \times 10^{-4}$ M; in absence of catalyst no deuteriation observed.

Rhodium is now the third metal, after platinum and iridium, found to catalyse exchange with organic compounds under both homogeneous and heterogeneous conditions. It is obvious that rhodium possesses certain unique properties in these reactions, a fact that is of great value when these catalysts are to be used as general deuterium and tritium labelling tools.[8] It is also becoming increasingly evident that there are a number of properties common to all three metals in these exchange systems. These trends give added support to the mechanistic role of π-complexes in homogeneous and heterogeneous metal-catalysed deuteriation reactions, especially the function of π-dissociative processes, confirmed by orientation effects, particularly with the alkylbenzenes such as *p*-xylene.

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