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Dimerization during *Heterogeneous* Platinum-catalysed Exchange of Aromatic Compounds with Isotopic Water. Advantages of a *Homogeneous* Labelling Procedure

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THE most useful one-step method for the general labelling of aromatic compounds with deuterium and/or tritium is *heterogeneous* platinum-catalysed exchange with isotopic water.[1] Recently an analogous *homogeneous* procedure with soluble platinum(II) salts has been discovered and developed for such labelling.[2]

Some dimerization of the parent compound, as a competing reaction to exchange, can be observed (Table) for a large number of aromatics only in the *heterogeneous* system. This is important because:

(1) In tritium labelling,[3] the presence of radioactive impurities renders difficult *radiochemical*, as distinct from *chemical*, purification of the parent compound. Normally only one exchange is necessary in tritium work and, under these conditions, the yield of dimer (Table) can be as high as 1%. Further, the isotopic enrichment in the dimer in the initial stages of the exchange is usually considerably higher than in the parent compound, and thus can complicate radiochemical purification.

(2) For deuteriation, high isotopic enrichment is usually required and this necessitates a number of equilibrations. To achieve this experimentally, the diluted heavy water, after each exchange cycle, is removed and replaced with 99·8% D_2O, then the system is allowed to attain equilibrium again. With this method of successive equilibrations, the dimer yield is autocatalytic and can be as high as 50% with compounds such as the polycyclic hydrocarbons (naphthalene, anthracene)[4] after four exchanges at temperatures of 130—150°. The dimerization can be minimized by purifying the hydrocarbon once after each cycle, then using fresh catalyst with the new charge of heavy water. For some compounds which are slow to exchange, *e.g.* naphthalene, increasing the temperature (from 120 to 150°) not only increases the rate of deuteriation, but also favours dimerization, since dimerization appears to possess a higher activation energy. With the labelling of such compounds, it is thus preferable to exchange for a longer time at the temperature to minimize the competing side-reaction.

(3) The observation of *heterogeneous* dimerization is important to fundamental catalytic theory. At present, some controversy exists as to whether *heterogeneous* exchange of aromatics occurs through associatively or dissociatively adsorbed intermediates.[5,6] In the current work, dimerization demonstrates that dissociatively adsorbed aromatic molecules are present in this exchange system. The dimerization may occur either indirectly as a consequence of π-complexing with oxygen (from dissociatively adsorbed water) on the surface of the catalyst, followed by loss of hydrogen to give, in the case of benzene, species (I), or directly from π-bonding with a surface site [species (II)] followed by a π–σ conversion as suggested in the dissociative π-complex substitution mechanism[5] for exchange. The fact that, from benzene, biphenyl is formed in systems where water is absent (Table, runs 10,11) suggests that oxygen from the water, either as species (III) or a disproportionation species (IV), is not exclusively responsible for initial phenyl radical formation by hydrogen abstraction. This conclusion involving the non-participation of species (IV) in the dimerization mechanism is supported by the fact that biphenyl is formed even at room temperature in the presence of water (Table) whereas oxygen, presumably as species (IV), is known to poison benzene exchange on platinum at this temperature (ref. 5; also Table, run 9). The further important observation in the reaction is that the exchange and the dimerization appear to be related since as the deuteriation increases, so does the yield of dimer, *e.g.*, Table (runs 1—3), after 2 hr. at 130°, the dimer yield is


(I)


(II)


$\overset{\displaystyle H}{\underset{\displaystyle Pt}{\overset{|}{\underset{|}{O}}}}$

(III)


$\overset{\displaystyle O}{\overset{\|}{Pt}}$

(IV)

Dimerization of benzene on platinum catalysts[a]

Run	Catalyst	Method of reduction	Additional reactants	Reaction temp. (degrees)	Reaction time (hr.)	Biphenyl (*w*/*w* %)
1	$PtO_2,2H_2O$	H_2	H_2O	130	2	0·004
2	$PtO_2,2H_2O$	H_2	H_2O	130	4	0·006
3	$PtO_2,2H_2O$	H_2	H_2O	230	96	1·3
4	$PtO_2,2H_2O$	H_2	D_2O	25[b]	336	0·09
5	$H_2PtCl_6,6H_2O$	$NaBH_4$	H_2O	130	96	0·8
6	$H_2PtCl_6,6H_2O$	H_2	H_2O	130	96	0·4
7	$PtO_2,2H_2O$	S.A.[c]	H_2O	130	96	1·3
8	$PtO_2,2H_2O$	H_2,O_2 poisoned then S.A.[c,d]	H_2O	100	96	0·4
9	$PtO_2,2H_2O$	H_2,O_2 poisoned	D_2O	25	336	0·0[e]
10	$PtO_2,2H_2O$	S.A.	0·0	130	96	1·3
11	$PtO_2,2H_2O$	H_2,O_2 poisoned then H_2 reduced[d]	0·0	130	96	0·06
12	Na_2PtCl_4	Homogeneous	—[f]	100	24	0·0

[a] Heterogeneous reaction conditions: benzene (3·0 ml.); water (3·0 ml.); catalyst for runs 1—4, 7—11 (0·12 g.); runs 5,6 (0·27 g.).

[b] Benzene deuteriated to equilibrium.

[c] S.A. = self-activation, defined as *in situ* reduction by the organic compound (refs. 1 and 5).

[d] Procedure involves initial reduction of bulk catalyst with H_2, then oxygen poisoning of this prereduced bulk followed by careful further scavenging of the oxygen (ref. 5).

[e] No deuterium in benzene after reaction. Compare with run 4.

[f] Reaction conditions as in ref. 2, *e.g.* AcOD (1·00 mole), D_2O (0·60 mole), Na_2PtCl_4 ($1·30 \times 10^{-3}$ mole), and DCl ($1·30 \times 10^{-3}$ mole).

0·004%; after 4 hr. at this temperaute it is 0·006% and at the end of 4 days it has reached 1·3%. Note also (Table, runs 4 and 9) that exchange of benzene occurs at room temperature together with biphenyl formation on a hydrogen pre-reduced catalyst (run 4). However, when this catalyst is oxygen-poisoned (run 9) neither exchange nor dimerization occurs.

(4) The final significant feature of the present work is that no competing dimerization (Table, run 12) has been observed in *homogeneous* exchange with platinum(II) salts as catalysts. This is a further advantage of the *homogeneous* procedure, particularly for tritium work, and, *where applicable*, it is recommended that the *homogeneous* method be used in preference to *heterogeneous* alternatives. Lack of dimerization also indicates that free uncomplexed phenyl radicals do not participate in the mechanism of the *homogeneous* reaction. The data thus support the π-complex mechanism suggested for the *homogeneous* exchange.[7]

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