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# A π-Complex Mechanism for Catalytic Exchange Reactions

The importance of π-complex intermediates has already been discussed in connection with the catalytic deuteration and tritiation of aromatic compounds (*1*, *2*). The existence of π-bonded species has also been proposed during the exchange of aliphatic hydrocarbons with deuterium (*3*). Extensive work involving typical π-electron systems, namely the monosubstituted benzenes (*1*), polycyclic aromatic hydrocarbons (*4*), and heterocyclics (*5*) has indicated that the exchange mechanism does not proceed by a *simple* π-complex substitution mechanism. The essential difficulty with such an interpretation is the failure to explain adequately ring orientation effects (*1*) and the ready exchange between two aromatic species. This conclusion is further substantiated by the results of exchange between deuterium and 7 alkylbenzenes on nickel (*6*) where ring hydrogens exhibit similarly drastic ortho deactivation effects.

In an extension of our monosubstituted benzene work, we have exchanged 12 alkyl aromatics and benzotrifluoride with deuterium oxide in the presence of active platinum (*7*, *8*), which differs from nickel in that aromatic and not aliphatic hydrogens are preferentially exchanged. Significant features of the results (Table 1)* indicate that: (a) The alkylbenzenes do not appreciably poison benzene exchange (*8*). (b) "Complete" ortho deactivation occurs when the ortho position is adjacent to a very large inert group or "flanked" by two methyl groups (*tert* butylbenzene, benzotrifluoride, mesitylene, and *m*-xylene). (c) "Severe" but incomplete *ortho* deactivation occurs when the *ortho* position is adjacent to only one methyl group. Isopropylbenzene is the one molecule which does not belong to either category, but appears to occupy a position midway between the two extremes. The relative reactivity of the alkylbenzenes in terms of active aromatic hydrogens is benzene > ethylbenzene > o-xylene > cumene > toluene > benzotrifluoride > *m*-xylene > *p*-xylene > hemimellitene > *tert* butylbenzene > mesitylene (no observed deuteration in the ring hydrogens of the last compound).

From these results and previously reported data (*1*, *2*, *4*, *5*), it is now possible to distinguish between two new mechanisms which the authors are postulating for catalytic exchange and propose to call the Associative and Dissociative π-Complex Substitution Mechanisms. Both mechanisms involve a π-complex-chemisorbed aromatic hydrocarbon which occupies a horizontal position on the catalyst surface [Eq. (1)]. When water or another aromatic is the other exchanging reagent, then π-complex bond

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* A more detailed account of this work will be published in the immediate future (*8*).

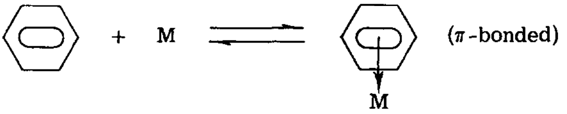
TABLE 1
EXCHANGE[a] BETWEEN ALKYLBENZENES AND HEAVY WATER

| Series[c] | Substance | Reaction time (hr) | % D in active aromatic hydrogens | $k_n$[b] % D ($hr^{-1}$) | Ionization potential | Active aromatic hydrogens |
|---|---|---|---|---|---|---|
| A | Benzene | 2 | 52.0 | .87 | 9.24 | 6 |
| A | Ethylbenzene | 4 | 58.5 | .58 | 8.76 | 5 |
| A | *o*-Xylene | 4 | 48.7 | .28 | 8.55 | 4 |
| A | Cumene | 4 | 42.9 | .26 | 8.68 | 5 |
| A | Toluene | 4 | 35.1 | .187 | 8.82 | 5 |
| A | *m*-Xylene | 4 | 27.9 | .112 | 8.56 | 3 |
| A | *p*-Xylene | 4 | 13.7 | .053 | 8.44 | 4 |
| A | *tert* Butylbenzene | 4 | 1.74 | .005 | 8.68 | 3 |
| B | Trifluorotoluene (benzotrifluoride) | 2 | 14 | .100 | 9.68 | 3 |
| B | Toluene | 2 | 16 | .136 | — | 5 |
| C | Hemimellitene (1,2,3 trimethylbenzene) | 24 | 9.2 | .053 | — | 3 |
| C | *tert* Butylbenzene | 24 | 47.1 | .039 | — | 3 |
| D | Mesitylene | 24 | 0.00 | 0.000 | 8.39 | 0 |

[a] All reactions performed at 120°C in the presence of active platinum (*7*).

[b] With respect to active aromatic hydrogens only.

[c] Refers to variations in reaction procedure, mainly catalyst preparation. Comparison in relative reactivity of compounds only possible within each series. For this purpose, Series A & D are essentially the same.



(I)

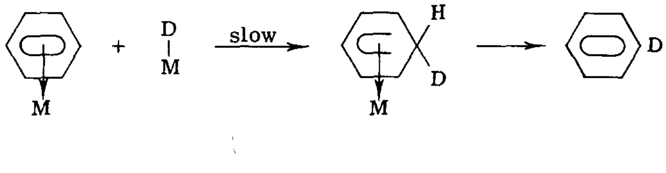
strength usually determines the reaction rate by influencing water surface concentrations through strong displacement effects. In the presence of Adams's platinum catalyst, heavy water, or deuterium gas exchanges readily with aromatic hydrocarbons and it is acknowledged that the former reagents supply chemisorbed deuterium atoms by dissociative chemisorption.

### *Associative π-Complex Substitution Mechanism*

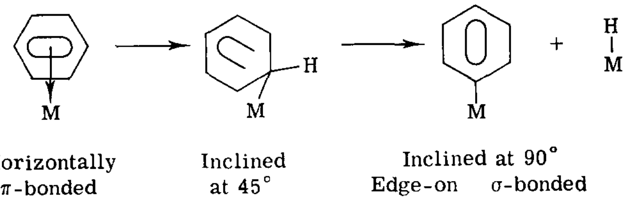
In this mechanism Eq. (2) the π-bonded aromatic nucleus is attacked by a chemisorbed deuterium atom; the transition state, except for the π-bonded aromatic, being essentially identical with conventional aromatic substitution reactions. Note the direction of the charge transfer, from the aromatic to the metal.

### *Dissociative π-Complex Substitution Mechanism*

In this mechanism the π-bonded aromatic reacts with a *metal radical* in a conventional type of substitution reaction which is rapid because of the π-complex intermediate. During this process, the molecule rotates through 90° and results in σ-bonded (edge-on) chemisorption (III). The postulated transition state for this π–σ bond conversion occurs at approximately 45° to the catalyst surface and is similar to that proposed by Melander (*9*) for homogeneous substitution reactions, namely out-of-plane bending of a carbon–

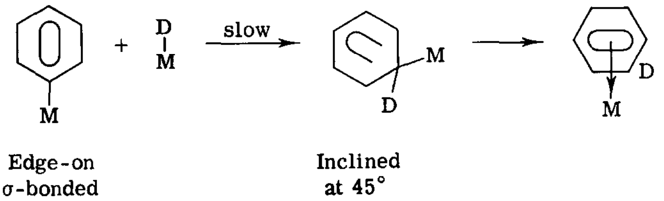


(II)



(III)

hydrogen bond. Furthermore, the formation of this state should be assisted by the asymmetric nature of the π complex (*10*). In the σ-bonded state, the aromatic undergoes a further but slower substitution reaction [D/T isotope effect of 1.6 (*8*)] with a chemisorbed deuterium atom Eq. (4).



(IV)

Present evidence suggests that the Dissociative π-Complex Substitution Mechanism is of major importance in platinum-catalyzed exchange reactions for the following reasons:

1. *Ortho* deactivation effects, determined by both infrared and mass spectrometry, in the alkylbenzenes (Table 1) and other molecules (1, 4) may now be interpreted satisfactorily. Since a π-bonded molecule must rotate through an angle of 90° to form a carbon–metal σ bond, a methyl substituent may exercise two different types of steric effects, i.e. it may hinder the formation of (i) the π complex and (ii) the σ bond. The former determines the reactivity of the sterically unhindered ring positions while the latter appears to be responsible for the orientation effect. Models clearly show that a *tert* butyl group or two *meta*-situated methyl groups prevent the *ortho* carbon from forming a σ bond with the metal, while such a bond is possible when only one methyl group is involved. In the latter case, steric hindrance is considerably decreased but remains effective enough to produce "severe" deactivation of the ring position.

2. The data from benzotrifluoride indicates that *ortho* deactivation is not caused by electronic effects of the substituent since the inductive effect is opposite to that of an alkyl group but produces the same deactivation as a *tert* butyl substituent.

3. In acid-catalyzed exchange of the alkylbenzenes, which proceeds by a conventional substitution mechanism ($D_3O^+$), there are no large steric hindrance effects observed (*11*), hence catalytic deactivation can only be explained by steric hindrance to the formation of the σ-bonded state of the proposed Dissociative Mechanism. Orientation effects are altered when the substituents are no longer inert, such as in aniline where electron lone pairs may influence charge-transfer adsorption (*5*, *8*).

4. Randomization reactions between non-isotopic and 100% deuterated benzene are equally as fast as exchange between benzene and water (*8*). It has been shown that the former can only occur if the aromatic hydrocarbon undergoes Dissociative Chemisorption, while its reaction rate, being identical to aromatic water exchange, suggests that the Associative Mechanism plays only a minor role (*7*).

5. The Dissociative π-Complex Substitution Mechanism is consistent with all previously published evidence (*12*) which at times could only be explained by either Classical Associative (*13*) or Classical Dissociative (*14*) theory.

6. The adsorption behavior of aromatic molecules substantiates π-complex chemisorption and is in qualitative agreement with Mulliken's charge-transfer theory (*15*).

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