THE PLATINUM-CATALYZED ISOTOPIC EXCHANGE REACTION OF AROMATIC COMPOUNDS

by

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PREFACE

The development of the science of catalysis resembles the progress of an autocatalytic reaction. About 1860, Berzelius formulated what appeared to be the starting point of the theoretical aspects of catalytic science with the expression "catalytic forces", and was followed by Faraday's experimental studies on the "power of metals and other solids to induce the combinations of gaseous bodies". However, progress was very slow until Sabatier made his important and numerous contributions to catalytic hydrogenation. This historical event in the chemistry of catalysis, really placed it on a firm foundation. Then, at the turn of the century, with the successful catalytic hydrogenation of fats and the high-pressure synthesis of ammonia, the science and technology of catalysis took a sharp upward turn. The basic contributions by Langmuir, around 1915, and the successful production of oleum, hard fats and ammonia by industry, opened the door to the progress noted during the last 40 years.

In general, the theory of catalysis has always followed its practical applications. It was during the third decade of this century after the discovery of deuterium that, for the first time, mechanisms of catalytic reactions appeared in the literature, thanks to the work of Farkas, Horiuti, Rideal and several others. They postulated the role of the catalyst in chemical reactions from the results obtained for gas phase deuterogenation and deuterium exchange of ethylene and ethane in the presence of nickel metal. But the actual picture of catalytic action on chemical reactions is still ambiguous in spite of the great amount of work already accumulated.

The fields of investigation can be classified according to the type of compound studied, namely, the aliphatic, the olefinic and the aromatic compounds, whether or not the reaction is homogeneous or heterogeneous, and occurs in the gaseous or the liquid phase.

The specific field of interest in this thesis is the study of the liquid phase heterogeneous exchange reaction between monosubstituted benzenes and deuterium oxide.

ACKNOWLEDGMENTS

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ABSTRACT

Partial protonation (10-12 atom% H) of a series of perdeuteriomonosubstituted aromatic compounds (98-99.5 atom% D) was effected by exchange with water in the presence of activated platinum metal. The products were subjected to analyses by mass-spectrometry and N.M.R. spectroscopy. From a knowledge of the amount of protium introduced in the ortho, meta and para positions, partial rate factors for each of a series of monosubstituted benzenes were calculated. A correlation was found with the A values reported in the literature for the steric effect of different substituents. No relationship between electronic factors and directive effects of the substituent was apparent. The data obtained are interpreted with respect to the most likely mechanism for the exchange reaction.

INTRODUCTION

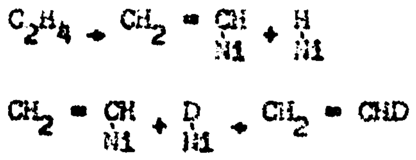
The procedure devised by Leitch (1) for the preparation of benzene-d_6 by the reaction of benzene with deuterium oxide in the presence of a platinum catalyst at 110° has been found to be superior to the vapor phase exchange on nickel at a higher temperature (2) and also to the older method based upon the exchange of benzene with deuterio-sulfuric acid (3) because it is more convenient and gives fewer by-products.

This method of deuteration was extended to substituted benzenes, heterocyclic and polycyclic compounds (4,5,6) and is used nowadays as a general method for introduction of deuterium in aromatic and heterocyclic compounds.

Several investigators realized that observations on this reaction could be of great value in the study of the mechanism of heterogeneous catalytic exchange reactions. It is the aim of this thesis to advance experimental facts in order to clarify this matter.

Before considering the present state of this recent field, it would be instructive to examine the proposed mechanisms of exchange of ethylene as this will serve to introduce many terms and concepts essential to a study of any catalytic exchange reactions.

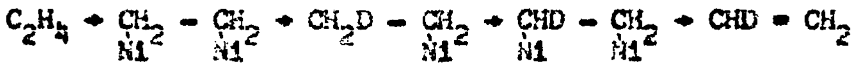
As early as 1933, Farkas and Farkas (7) proposed a dissociative mechanism for the catalytic exchange reaction between deuterium and olefins (Eq. 1). But in 1934, Horiuti (8) disagreed with this dissociative mechanism and presented evidence supporting an associative mechanism (Eq. 2).



$$C_2H_4 \rightarrow CH_2 = \underset{\text{Ni}}{CH} + \underset{\text{Ni}}{H}$$

$$CH_2 = \underset{\text{Ni}}{CH} + \underset{\text{Ni}}{D} \rightarrow CH_2 = CHD \qquad (1)$$

Dissociative Mechanism



$$C_2H_4 \rightarrow \underset{\text{Ni}}{CH_2} - \underset{\text{Ni}}{CH_2} \rightarrow CH_2D - \underset{\text{Ni}}{CH_2} \rightarrow \underset{\text{Ni}}{CHD} - \underset{\text{Ni}}{CH_2} \rightarrow CHD = CH_2$$

Associative Mechanism

The associative mechanism was further supported by the experimental work by Twigg (9, 10). He failed to observe a randomization of deuterium when light ethylene C_2H_4 and deuterated ethylene C_2D_4 were allowed to interact on a nickel filament as catalyst under conditions where exchange between ethylene and deuterium was quite rapid.

In addition, the calculation of the heat of chemisorption by Eley (11) favored the adsorption as

$$\underset{\text{Ni}}{CH_2} - \underset{\text{Ni}}{CH_2}$$

However, Koidzumi (12) reported that Twigg's failure to observe exchange in this system was at least partly due to the small surface area used. Exchanges between ethylene-d_4 and propylene or butenes were subsequently detected using nickel powder even at 45°. The same result was obtained by Amand (13) between ethylene and deuterated 1-butene and 2-butene using

Raney nickel and palladium, by Douglas and Rabinovitch (14), between ethylene and ethylene-d_4 on nickel wire or nickel-Kieselguhr at room temperature, and finally, by Flanagan and Rabinovitch (15) who obtained complete equilibrium over an evaporated nickel film at 23° in less than an hour.

The significance of these observations can be questioned since the nature of adsorbed hydrogen on the surface of the catalyst was not known and no actual proof was given that no residual hydrogen was still chemisorbed on the catalyst.

More information was obtained by Turkevich (16), followed by Wilson (17), when they obtained complete analyses, from mass-spectrometer techniques, of the products of exchange between ethylene and deuterium gas using nickel wire or pelleted nickel on kieselguhr as catalyst. From their work, a complete series from ethane-d_0 to ethane-d_6 was obtained, which lead them to conclude that exchange and deuterogenation of ethylene are closely related reactions, but that the hydrogen redistribution reaction was much more rapid than alkane-formation, i.e. the average residence time of a hydrocarbon entity on the surface must have been long enough to establish the steady-state distribution of deuterated species among the adsorbed hydrocarbon species before desorption as alkane occurred.

Kemball (18) studied the gas phase exchange and deuterogenation reactions of deuterium and ethylene, and found a correlation between the extent of deuteration and the distribution of the deuterium introduced into the hydrocarbon. He concluded that the reaction was proceeding from an adsorbed ethylene to an adsorbed ethyl radical. This adsorbed ethyl radical must either revert to the adsorbed ethylene molecule or leave the surface as an ethane molecule.

A marked difference was noticed between the exchange of ethylene and the exchange of ethane for which the catalyst showed widely different activities. This observation is by itself supporting evidence that the slow step in the exchange of ethane is the dissociative adsorption of the molecule.

The theory advanced for ethylene was extended to the benzene-deuterium system and it was postulated that exchange and deuterogenation were occurring simultaneously and an adsorbed phenyl radical was playing an important part in the reaction (19).

Furthermore, it was found that the distribution in benzene did not follow equation 3 which expresses random deuterium distribution for a simple exchange mechanism.

$$D^n = \frac{a!}{a!(a-n)!} x^n (1-x)^{a-n} \qquad (3)$$

where D^n is the fractional abundance of the organic molecule containing 'n' deuterium atoms and having 'a' exchangeable protons.

x and (1-x) are the fractional abundances of hydrogen and deuterium atoms in the hydrogen phase at time 't'.

Instead, a non-random distribution of deuterium was found which was interpreted as arising from a second multiple exchange mechanism. In multiple exchange, a parameter 'M' may be calculated corresponding to the mean number of deuterium atoms entering each benzene molecule under the initial conditions. This parameter is defined by two rate constants

$$M = \frac{k_\phi}{k_0} \qquad (4)$$

k_ϕ is the initial rate of entry of deuterium atoms into 100 molecules of benzene-d_0. It can be obtained from the function ϕ, which is the measure of the total deuterium content of the products as defined by equation (5).

$$\phi = 1d_1 + 2d_2 + 3d_3 + 4d_4 + 5d_5 + 6d_6 \qquad (5)$$

where d_1 to d_6 represent the percentage of total benzene present as benzene-d_1 to benzene-d_6.

The ϕ function varied in most reactions with time according to the first order equation,

$$\frac{d\phi}{dt} = \frac{k_\phi}{\phi_\infty} (\phi_\infty - \phi) \qquad (6)$$

or, on integration, by

$$-\log_{10} (\phi_\infty - \phi) = \frac{k_\phi t}{2.303\, \phi_\infty} - \log_{10} \phi_\infty \qquad (7)$$

ϕ_∞ is the final value corresponding to equilibrium.

k_0 is an empirical relationship for the initial rate of disappearance of benzene-d_0 in % with 't', and it is assumed to be valid for a considerable range of exchange reactions by the equation

$$-\frac{db}{dt} = \frac{k_b\,(b - b_\infty)}{(100 - b_\infty)}$$

or, integrating

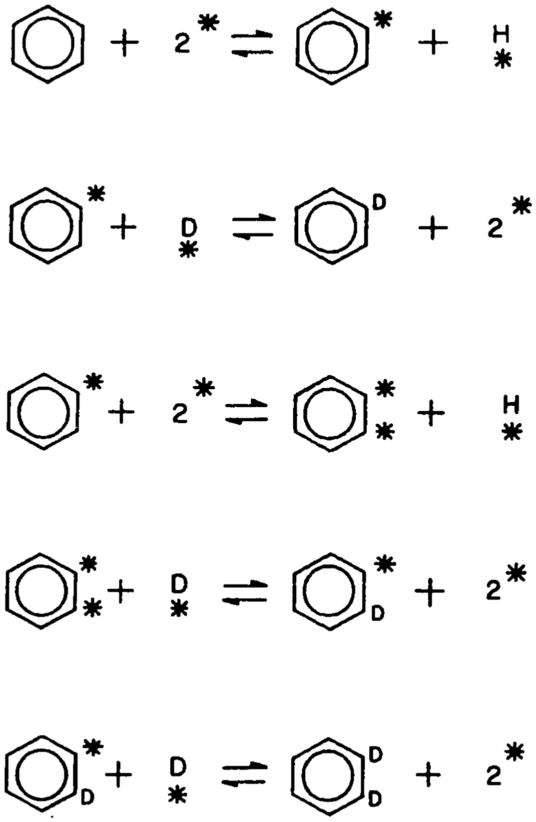
$$-\log_{10}(b - b_\infty) = \frac{k_b t}{2.303\,(100 - b_\infty)} - \log(100 - b_\infty) \qquad (9)$$

where 'b' is the percentage of the total benzene present as benzene-d_0 at time 't' and 'b_∞' is the equilibrium value of 'b'

For a simple exchange reaction where only one atom of hydrogen is introduced at a time, M is equal to 1, but for multiple exchange, M is greater than 1.

These observations suggest that the exchange reaction between benzene and deuterium in the presence of platinum catalyst did not proceed by a simple exchange mechanism, having both rates equal, but also by a multiple exchange mechanism. This could proceed by a "repeated second-point adsorption" involving a further dissociative adsorption of adsorbed phenyl radical to form adsorbed phenylene radical (Eq. 10).

$$D_2 + 2^{*} \longrightarrow 2\,D^{*}$$

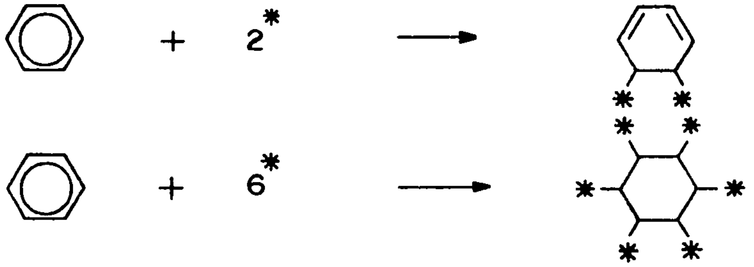


Equation 10

Note: * = active catalyst site and will be used throughout the text to indicate such a site.

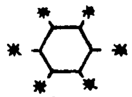
On the other hand, it seems generally agreed that aromatic compounds lose their energy of resonance on adsorption. The relative magnetization of supported nickel falls when benzene is chemisorbed upon it at 150° to an extent which suggests that it is held to the surface by at least six bonds. (20)

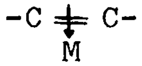
While this observation would tend to discount the possibility that benzene is only chemisorbed dissociatively, that is, as a phenyl radical and a hydrogen atom, it does not distinguish with absolute certainty between the alternative possible processes of associative adsorption, viz. (Eq. 11),



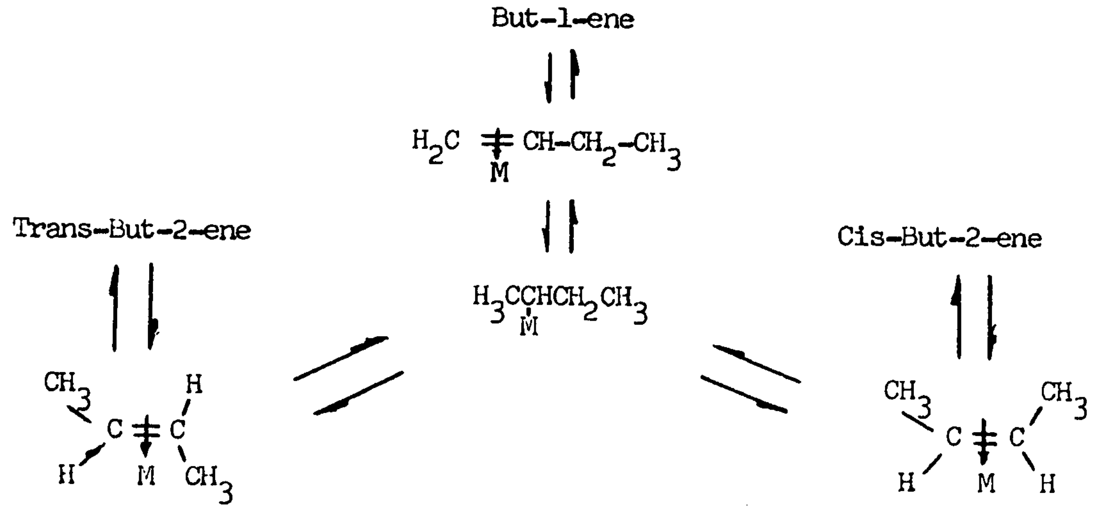
(11)

in both of which the resonance energy would be largely lost.

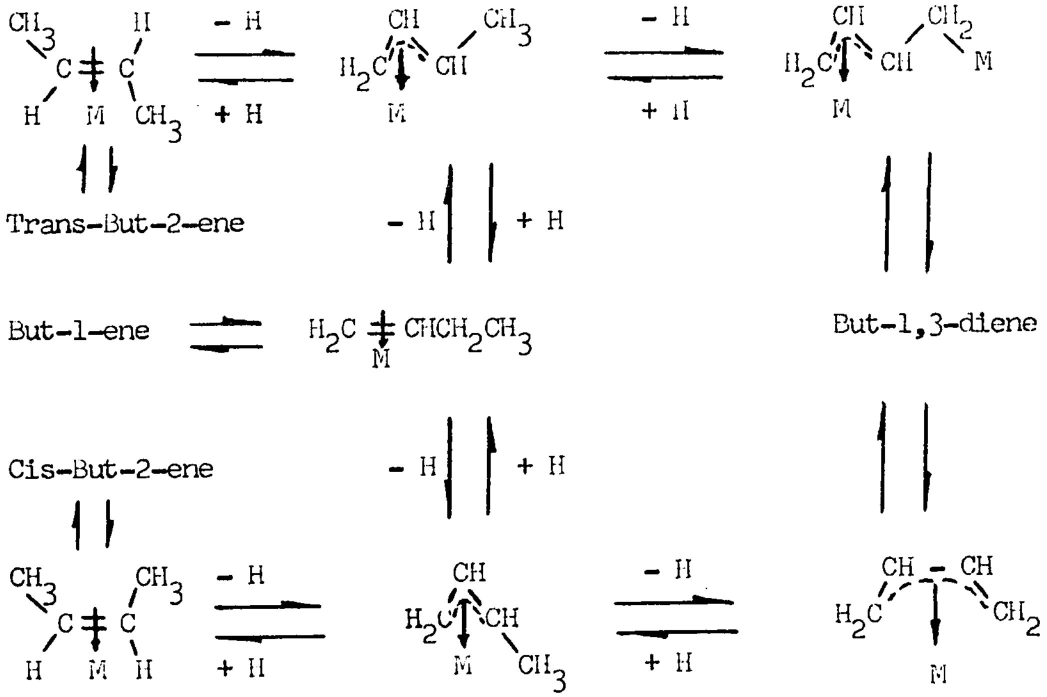
Burwell (21) approved the possible existence of  in the absence of hydrogen but its participation in reactions has not been conclusively proved.

These results really stimulated interest in this very important field of chemistry which was very slow to start. Kemball (22) and Rooney (23) developed a new mechanistic theory in order to explain several reactions of hydrocarbons on metal catalysts. Using mass-spectrometric analytical technique, they postulated that reactive hydrocarbons containing three or more adjacent nonquaternary carbon atoms can form a π-bonded complex on the surface of group VIII transition metals, consisting of a olefinic electron donor to a metal acceptor which can be represented by  $-C \underset{M}{\overset{}{\downarrow\!\!=}} C-$

According to Rooney and Webb (24), the isomerization of olefins can be explained using the π-complex intermediate between the electron donor ligand and the electron acceptor metal catalyst such as platinum, palladium, nickel and rhodium. Two possible mechanisms have been proposed for the double-bond isomerization of n-butene, namely interconversion between olefinic and alkyl intermediates and interconversion between olefinic and π-allylic complexes. These mechanisms are shown in Eq. 12 and 13.



Equation 12



Equation 13

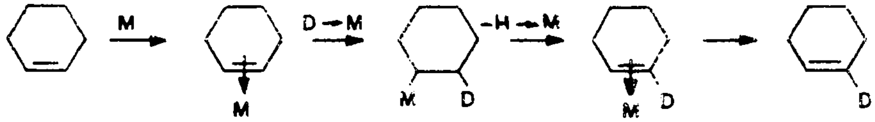
This π-complex formation was emphasized since the discovery of ferrocene, and the results obtained from the measurements of the surface potential of the complexes formed. According to Mignolet (25), when acetylene and ethylene were adsorbed on nickel films at 20°C, positive potentials of 1.00 and 0.83 volt respectively developed. These values suggest that there is strong donation of charge from the π-orbitals of the hydrocarbons to the acceptor orbitals of the metal.

Furthermore, Bond (26) mentioned a lack of correlation between the ease of a σ-bonding formation of acetylene and ethylene, and the rate of hydrogenation of acetylene and ethylene which depend on some geometric restriction in the formation of a σ-bonded metal to acetylene and ethylene, and suggested that this restriction is not involved with the formation of a π-complex.

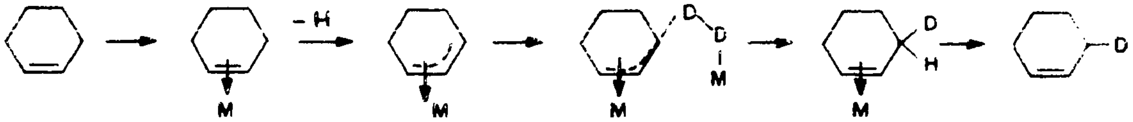
Even though no direct evidence for the two types of intermediates has been obtained, in many cases there is more indirect evidence for the π-bonded intermediate over the σ-bonded one. But it is also believed that both intermediates can participate depending on the nature of the catalyst and the organic ligands.

Another case where the π-complex mechanism has been considered is the exchange reaction between cyclohexene and deuterium in presence of a metal catalyst (24).

Two mechanisms are possible:



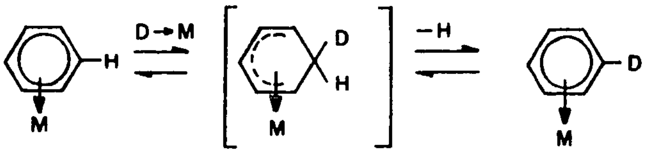
Equation 14



Equation 15

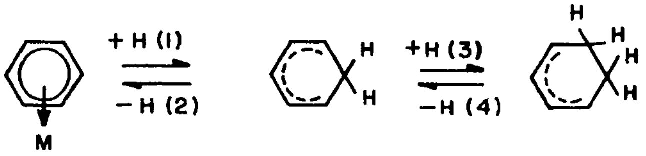
The first one (Eq. 14) consists in the reaction of a chemisorbed metal catalyst on the π-electrons of the olefinic group with a chemisorbed deuterium as atomic complex on the metal to form a σ-bonded metal cyclohexane, which, by abstraction of an active hydrogen chemisorbed on the surface of metal, gives the exchange product. Or, the allylic proton of the π-complex (Eq. 15) can be adsorbed dissociatively by a metal catalyst to give an allylic π-complex intermediate which can react with an activated molecule or atom of deuterium to give the exchange product. The first mechanism should be reserved for ethylene-like compounds, but whenever an allylic system is possible, the second mechanism should be more likely due to a greater delocalization of the electrons in the transition state.

This π-complex mechanism was extended by Rooney and Webb (24) to the heterogeneous catalytic exchange of benzene and deuterium (Eq. 16). It consists in the reaction of an activated chemisorbed atom or molecule of deuterium and a chemisorbed benzene-metal complex to form an sp^3 hybridized carbon intermediate which, upon abstraction of a hydrogen atom by the catalyst, gives the exchanged product.



(16)

Hence, the only difference between the mechanisms of exchange and hydrogenation reactions is that for hydrogenation, the addition of hydrogen is faster than its removal. In equation 17, the slow step in exchange is the addition of hydrogen (step 1), whereas the slow step in hydrogenation is the addition of a second hydrogen (step 3) and so on.



(17)

The lifetime of the C_6H_7 π-complex is an important factor. The more labile the cyclohexadienyl π-complex will be, the more readily it will dissociate back to benzene. Two main factors may contribute to this behavior. The first one is the nature of the metal itself. The ratio of rate of hydrogenation and exchange reactions increases from nickel, palladium and platinum. Secondly, from the nature of the ligand, an increase in electron density of the benzene ring by substitution of alkyl groups for hydrogen increased the stability of the cyclohexadienyl π-complex and at the same time increased the rate of hydrogenation.

Unfortunately this mechanism proposed by Rooney is not in agreement with the results obtained by Kemball (19) who claimed to have very good evidence that the exchange and deuterogenation of benzene are quite independent. This was based on three observations which can be summarized as follows:

a) The rates of exchange and deuterogenation are different.

b) The redistribution of deuterium in deuterogenation, a phenomenon observed in ethylene and ethane, is absent. No low deuterium content in the cyclohexane is formed, i.e. the exchange is not permitted to occur during the process of deuterogenation.

c) No inhibition of deuterogenation by cyclohexane was taking place because of the constant rate of production of total cyclohexane while, on the other hand, the exchange reaction on palladium was retarded by cyclohexane.

Kemball concluded from these observations that two entirely different mechanisms operate for exchange and deuterogenation reactions.

Völter (27) investigated the relation between rate and ionization potential of a series of alkylated benzenes in order to examine the likelihood of formation of a π-complex intermediate of the type proposed by Rooney and supported by Kemball. He noticed from the sequence of the activation energies of hydrogenation of the benzenes in vapor phase on Ni-MgO as catalyst that the hydrogenation was facilitated by increasing the alkylation (Table I). This can be explained by a reduction in the ionization potential with an increase of the alkylation of the ring and, as a result, the formation of a charge-transfer complex is promoted.

Substance	Activation energy of hydrogenation (Kcal/mole)	Ionization potential (e.v.)
Benzene	14.2	9.24
Toluene	13.5	8.82
Ethylbenzene	10.4	8.77
p-Xylene	11.1	8.44
Mesitylene	8.0	8.39

TABLE I

Obviously, more detailed information about the precise nature of the metallic bond is required before full adoption of the π-complex intermediate is possible. But, nevertheless, it seems reasonable to say that the aromatic type compounds form a π-complex in the first step of exchange and hydrogenation reactions.

The discussion up to this point was to show that three types of adsorption of unsaturated organic compounds on catalysts have been proposed, namely, the dissociative, the associative and the π-complex adsorptions, all of which have been considered as intermediates in exchange and hydrogenation reactions.

The remaining discussion will be devoted to the liquid phase platinum and nickel catalyzed exchange reaction of aromatic compounds and deuterium oxide.

Garnett was certainly the pioneer in this field of investigation. The first information he obtained (4) was the position of exchange in substituted benzenes using platinum as catalyst. He examined the products of exchange of sodium benzoate, benzoic acid, bromobenzene, nitrobenzene, p-nitrobenzoic acid and trimesic acid by infra-red spectroscopy, and noted that the protons of the ring were not exchanging at the same rate. Later, Garnett and Sollich (5) reported that for platinum catalyzed exchange between heavy water and the monohalogenated benzenes, the rate of exchange decreased with increasing size of the halogen substituent and also, that the proportions of ortho exchange increased with increasing size of the halogen substituent. Subsequently, Garnett (28, 29) obtained a relation between the extent of deuteration of benzene, pyridine, pyrrol, thiophene, phenol and anisole and their ionization potentials. He found that the lower the ionization potential of the organic ligand, the faster the exchange reaction proceeded. On the other hand, whenever these ligands were exchanged in presence of lower ionization potential compounds, such as anthracene, bibenzyl, phenanthrene and naphthalene, a large poisoning effect was noticed. This poisoning effect was explained by the greater adsorption ability of the catalyst on the surface of low ionization potential compounds, reducing at the same time the rate of exchange for those compounds of higher ionization potential.

Tiers (30) took advantage of the newest development in instrumental technique for analysis, N.M.R. spectroscopy, to determine the orientation effect in catalytic deuteration through a method which he called massive deuteration. Since the assignment of N.M.R. peaks to hydrogens at various positions had already been made, it was a simple matter to determine the amount of residual protons in the ortho, meta and para positions of the molecule. Examples of the orientation effect are listed in Table II.

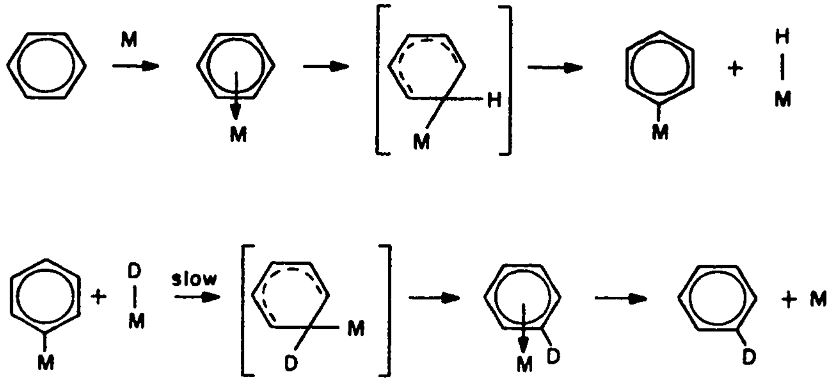
This method of analysis showed great promise in analyzing products of deuterium exchange reactions. The only difficulty lies in the analysis of protons with very small differences in chemical shift due to the low concentration of the proton remaining in the sample and also to the electric quadrupole moment of deuterium which causes the protons spin-coupled to it, to give slightly broadened lines. This last effect can be eliminated by an H-D spin-decoupler. This consists of an r.f. unit operating at 9.2 Mc which when turned on will cause transitions between nuclear energy levels of the deuterium nuclei to occur sufficiently rapidly that they can no longer interact with the protons whose spectrum is being recorded (56).

The main objection to the results of Tiers is that only a very crude estimation of the orientation effect in exchange reaction was obtained. In phenol, for instance, the greater activity of the meta protons over the ortho and the para protons can be argued as being due to the massive deuteration which extended the exchange reaction to equilibrium. The results obtained by Tiers then, are not too accurate.

Compound	Atom %D in ring	Position	Atom %D
Na Benzoate	90	ortho	90 ± 2
		m + p	90 ± 2
Na Benzoate	70	ortho	57 ± 2
		m + p	79 ± 1
Na Benzoate	61	ortho	26 ± 1
		m + p	84 ± 1
Phenol	52	meta	63 ± 1
		o + p	45 ± 1
Pyridine	35	α	53 ± 2
		β + γ	23 ± 1

TABLE II

Garnett and Sollich (31) indicated that the exchange mechanism does not proceed by a simple π-complex substitution mechanism (Eq. 15), because of the failure to explain adequately the ring orientation effect. They considered two likely mechanisms for the hydrogen exchange reaction between aromatic molecules and deuterium oxide. The first one is essentially the same as Rooney's (24), which they called the associative π-complex substitution mechanism. The second one, which they called the dissociative π-complex substitution mechanism, consists of initial formation of a benzene molecule chemisorbed as π-complex on the surface of the catalyst. In the next step the ring rotates to an angle of 90° on the surface of the catalyst to give a σ-bonded (edge-on) chemisorption, and the transition state for this π-σ-bond conversion occurs at approximately 45° to the catalyst surface. In the σ-bonded state, the aromatic ring undergoes a rate-determining substitution reaction with a chemisorbed deuterium atom (Eq. 18).

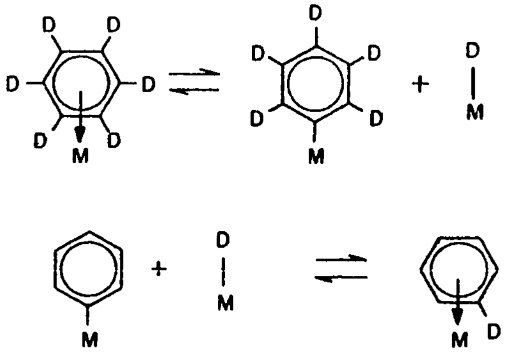


(18)

The authors concluded that the Dissociative π-complex Substitution Mechanism is of major importance in platinum-catalyzed exchange reaction because it explains better the ortho deactivation effects in alkylbenzenes. A π-bonded molecule must rotate through an angle of 90° to form a carbon-metal σ-bond, and due to steric effects, the formation of a π-complex or a σ-bond is hindered. Garnett also mentioned that the same ortho deactivation was noticed in the case of benzotrifluoride, and concluded that the deactivation is not caused by electronic effects since the inductive effect of an alkyl group is opposite to the effect of a trifluoromethyl group.

Garnett used infra-red spectroscopic and mass-spectrometric analysis techniques to determine the ortho effect in a series of alkyl benzenes. Unfortunately, analysis by this means is not too conclusive because no actual indication is given of the amount of deuterium introduced in the ortho positions. The ortho effect was deduced from the impossibility of exchanging mesitylene which has three hindered ring protons. It was found by Demayo (32) that deuterium could be introduced relatively fast in mesitylene. With these unreliable results, no definite conclusion can be made for the non-electronic participation in this type of exchange reaction. A more accurate determination of the relative amount of deuterium in different positions of the ring of the exchanged product is needed.

Garnett and Sollich-Baumgartner (33) added two further results in support of the dissociative π-complex mechanism. The first observation was that benzene-d_6 exchanged its deuterium with normal benzene in presence of platinum catalyst which was activated as follows: a large stock of platinum oxide ($PtO_2.2H_2O$) moistened with water was reduced with hydrogen for 48 hours at 30^oC, then exposed to the oxygen of the atmosphere in order to poison the active catalyst and, finally, a portion of this stock was activated at -90^o for 12 minutes in an atmosphere of hydrogen and then evacuated to a pressure of 0.006 mm at 100^o. Since a π-complex chemisorbed benzene cannot furnish any deuterium atoms to the catalyst and the associative mechanism required a second substrate, as deuterium oxide or deuterium gas, the deuterium must come from the dissociative mechanism. (Eq. 19)



(19)

They also found that the rate of randomization is very close to the rate of deuterium exchange and concluded that both reactions have to proceed through the same mechanism.

The second observation is based on the fact that the catalyst undergoes marked change in physical appearance during benzene-water exchange reactions; the catalyst being transformed from a coarse and coagulated powder into a finely divided film-like state. According to Garnett, both reagents have to be present in order to get this physical change.

The two observations made by Garnett are not entirely valid because they are based on a postulate which could be wrong. Plisken and Eischens (34) obtained actual proof by infra-red spectroscopy that activated platinum still retained a large amount of σ-bonded hydrogen adsorbed on its surface even after exposure to high temperature or low pressure. These σ-bonded hydrogens may very well exchange with the organic ligand through a hydrogen radical via an associative mechanism. The transformation of the physical appearance of the catalyst which was observed only when deuterium oxide was present in the exchange of benzene, is in contradiction with the randomization of deuterium in a mixture of benzene and deuteriobenzene in absence of water which is supposed to proceed through the same reaction mechanism.

Macdonald and Shannon (35) disapproved of the dissociative π-complex substitution mechanism proposed by Garnett, because of the results they obtained from the exchange reaction between isoquinoline or quinoline and deuterium oxide in presence of nickel on kieselguhr. They found that isoquinoline exchanged faster in the 1 and 3 positions than elsewhere, and quinoline exchanged in positions 2, 7 and 8 at a much faster rate than in the other positions. They concluded that the dissociative mechanism would predict a slower exchange of hydrogen atoms ortho to the substituents.

It is certainly unfair at this stage to criticize the dissociative mechanism solely on the basis of the results obtained by Macdonald since he worked with a different catalyst and substrates. Isoquinoline and quinoline were not appropriate for a criticism of the dissociative mechanism because they contained an atom rich in electron donating power to the catalyst, placing this one in a closer vicinity to the positions exchanged. This same behavior was also noticed for aniline and phenol when exchanged in presence of platinum and deuterium oxide. The associative mechanism would also predict a faster exchange of the ortho protons of the compounds studied. Until more data are obtained on the nature of the catalyst on different substrates, not too reliable comparison can be made between different catalysts.

Garnett (36, 37) reported a new process of activation of platinum oxide, which he called self-activation. It involved the reduction of Adam's catalyst ($PtO_2.2H_2O$) by organic compounds at a temperature higher than 120°C.

The results were promising for aliphatic compounds such as n-octane but relatively poor for benzene and naphthalene. Nevertheless, deuterium was introduced, but the mechanism of this reaction is certainly different from the reaction using platinum black. Because of the greater polarity of the oxide surface, the possibility of hydrogen abstraction could be effected via an oxygen radical.

Before closing this historical résumé, it may be worth while to mention briefly the work which was done on exchange reactions between alkylaromatic hydrocarbons and deuterium oxide or deuterium gas in presence of a nickel-catalyst and compare the mechanism of reaction proposed with the mechanisms of exchange reaction obtained using platinum catalyst.

In the work of Hirota (38) on the reaction between p-xylene and heavy water, that of Macdonald and Shannon (39), on reactions between alkylaromatic hydrocarbons and toluic acid derivatives with deuterium oxide, and finally, that of Horner and Mayer (40), on reactions between alkylbenzenes and deuterium gas, a close relation between the results obtained using platinum was found. Both the associative and the dissociative mechanisms were implied to fit the results obtained.

Nearly all the theory outlined till now on the mechanism of heterogeneous deuterium exchange reactions is largely qualitative. A few minor quantitative contributions only increased the confusion already existing between the different mechanisms of reaction proposed. It is the object of this thesis to present more reliable quantitative data which could lead to a better understanding of the nature of the reaction and its mechanism.

The line of thought followed was to take advantage of the newest developments in analytical methods, namely high-resolution N.M.R. spectroscopy and the more accurate mass-spectrometric technique. In order to simplify the interpretation of data by N.M.R. and mass-analyses, it was advantageous to work with highly deuterated monosubstituted benzenes. A series of monosubstituted deuteriobenzenes was chosen to illustrate the effect of the substituent in the heterogeneous protium exchange reaction. The results obtained were compared with other results reported in the literature on the nature and mechanism of the reaction.

The general procedure was to introduce the order of 10 atom% of protons into several monosubstituted benzenes which contained over 98.8 atom% deuterium initially. (Table III). The products were analyzed by mass-spectrometry and N.M.R. spectroscopy.

EXPERIMENTAL

DESCRIPTION OF THE APPARATUS FOR EXCHANGE REACTIONS.

All exchange reactions were carried out in a home-made rocking furnace consisting of a metal tube with both ends blocked with screwed metal caps. The tube was heated by means of an electrical filament wound around the tube and insulated with asbestos for minimization of heat loss. The temperature inside the tube was calibrated to a precision of $\pm 2^\circ$ over a range 50° to 220° by means of a thermometer inserted inside the tube. The temperature was varied by regulation of the current through the filament by means of a Variac. The tube was fixed at the center by a shaft, and was rocked by means of an arm which was attached to an electrical motor.

The reactions were carried out in sealed pressure glass tubes, 12 cm. long and 2 cm. in diameter, which were placed inside the metal tube.

ANALYTICAL METHODS.

1) Vapor phase chromatography (V.P.C.).

The purity of the liquid compounds were determined by a Perkin-Elmer model 154 vapor phase chromatograph, on a 2 meter column packed with silicone grease on diatomaceous earth. The analyses were done on the neat compounds.

2) Mass-spectrometry.

The mass-spectrometric analyses were done by two types of mass-spectrometer. The first one was a home-made apparatus built by Dr. F. P. Lossing of the National Research Council of Canada and the second one was a Hitachi model RMU-6D. Each instrument possessed the same accuracy for the nature of compounds analyzed. The analyses were done at low voltage (7.5 to 9 volts) in order to suppress dissociation processes. The deuterated species were determined by means of their parent peaks, which were first corrected for the carbon-13 contribution from the parent of next lowest molecule weight. The small isotopic effect (41) was neglected since the analyses were done on compounds of low proton content.

3) N.M.R. spectroscopy.

N.M.R. spectroscopic analyses were done on two types of spectrometer. A Varian A-60 model was used for qualitative analyses of deuterium content in the aromatic rings. This determination was done on the neat compounds whenever possible. A high-resolution Varian V-4302 model with a N.M.R. specialties spin decoupler was used for the determination of the relative amount of hydrogen in the ortho, meta and para positions and also to find the chemical shift of the protons in different positions on the ring relative to benzene in cyclohexane.

PREPARATION OF THE CATALYST.

The platinum black catalyst for the partial protonation of deuterated monosubstituted benzenes was prepared under the same conditions for every reaction.

Adam's catalyst ($PtO_2.2H_2O$) (12.5 mg) was placed in a pressure bottle with a pipetted quantity of distilled water (2.0 ml). The bottle was attached to a hydrogen apparatus and evacuated to 18 mm pressure and then the catalyst was activated by shaking during 10 minutes under 12 pounds pressure of hydrogen. The resultant suspension was then transferred directly to the container in which the exchange reaction was carried out.

ANILINE-d_7

Aniline, freshly distilled, (35 g) was exchanged with 50 ml of D_2O (99.7 atom% D) in the presence of activated platinum (0.1 g) in a sealed glass tube at 140°C for 3 days in the heated rocking furnace. Then the tube was cooled in ice and opened. The supernatant water was siphoned out and the heavy oil was transferred into another tube containing heavy water (50 ml) and platinum black (0.1 g), and heated as before. This process was repeated four times.

The material from the fourth exchange was distilled in a Späth bulb attached to a vacuum line. A yield of 25 g (71.4%) was obtained and the product analyzed 100% pure by V.P.C.

The product analyzed 99 atom% D by N.M.R. spectroscopic analysis. Unfortunately, the mass-analysis on the product could not be done due to the fragmentation of the molecule even at low voltage and also, due to exchange during the analysis, a phenomenon which is always noticed with compounds having labile protons. The deuterium content of the aniline-d_7. It is by mass-analysis on the chlorobenzene prepared from this analine-d_7. It is known that no loss of deuterium from the aromatic ring occurs during the Sandmeyer reaction under carefully controlled conditions (42).

CHLOROBENZENE-d_5.

Aniline-d_7 (3.1 g) placed in a 100 ml round bottom flask equipped with a magnetic bar stirrer, was cooled at -10°C with an acetone-dry ice bath. A solution of 8.5 ml of concentrated hydrochloric acid in 8.5 ml of water was slowly added. To this solution was added dropwise a solution of 2.4 g of $NaNO_2$ in 5 ml of water until a positive test with potassium iodide-starch paper was obtained. This solution, which was kept cold, was added in portions to a well-stirred solution of cuprous chloride in 17 ml of concentrated HCl at 8°C. The cuprous chloride was prepared according to the method described in Vogel (43). The mixture was allowed to warm up to room temperature, at which temperature the solid complex decomposed. After stirring for 1/2 hour, the chlorobenzene was distilled out with steam, extracted with ether, washed with 10% NaOH solution, followed by water, dried over $MgSO_4$ and filtered. The ether was removed under reduced pressure on a vacuum line. The residue, having a vapor pressure of about 0.1 mm, was distilled in a Späth bulb. The distillate (2.3 g, 63.2%) analyzed over 99.7% purity by vapor phase chromatography.

Mass-analysis: 94.2 mole% d_5 and 5.8% d_4.

or 98.8 atom% D.

PARTIAL PROTONATION OF CHLOROBENZENE-d_5.

The procedure described below for the partial protonation of chlorobenzene-d_5 was strictly followed for the partial protonation of all monosubstituted benzenes-d_5.

Chlorobenzene-d_5 (0.50 g) was introduced into a heavy walled pyrex tube. The suspension of activated catalyst was then added to the tube and the catalyst container was rinsed several times with small amounts of water until the total volume of water in the tube amounted to 5 ml. The tube was attached to a vacuum line, cooled in ice, evacuated to 10 mm pressure and sealed at a constriction. The mixture was heated at 110° for 18 hours in the rocking furnace.

The organic compound was then extracted with ether, dried over $MgSO_4$ and filtered into a Späth bulb. The ether was removed slowly under reduced pressure. This can be effected by opening the stopcock to a trap in liquid nitrogen in order to have a very slow leak. The vapor pressure of the residue can be measured at any time during the distillation. The residue (0.4 mm pressure at room temperature) was collected in one of the bulbs cooled in dry ice. The yield of distillate was 0.37 g (74%).

Mass-analysis: 54.5 mole% d_5, 34.4% d_4, 9.5% d_3 and
1.6% d_2, or 88.3 atom% D.

The aqueous layer was very slightly acidic and a positive test was obtained for chloride ions with silver nitrate in dilute nitric acid solution.

FLUOROBENZENE-d_5.

Aniline-d_7 (5 g) in a 100 ml round bottom flask was diazotized with 3.92 g of $NaNO_2$ in 8.0 ml of water as described for the preparation of chlorobenzene. To the diazonium salt was added in portions a cold solution of fluoroboric acid (prepared from 9 g of 48% hydrofluoric acid and 3.6 g of boric acid). Stirring was continued throughout the addition. Then, with occasional stirring, the medium was allowed to stand for 1/2 hour. The solid complex was collected in a sintered glass funnel, washed with 7 ml of cold water, followed by 5 ml of cold methanol and 7 ml of cold ether and finally dried in air overnight.

The dry salt, which weighed 7 grams, was placed into a 50 ml 2-necked flask to which was attached in series a condenser, a trap cooled in ice and a funnel dipping into a solution of 10% KOH solution. The air was displaced by dry nitrogen and the flask was heated gently with a small luminous flame at one point of the surface of the solid until decomposition began. From time to time the heating was resumed to keep the reaction going. At the end, the flask was heated more strongly while still passing nitrogen into the system. The distillate was washed twice with 10% NaOH solution and dried by distillation through anhydrous $CaCl_2$ in a U tube attached to a vacuum line.

The dry distillate (2.7 ml, 68.6%), which was stored in a freezer in a well stoppered vial, was shown to be 100% pure by V.P.C.

Mass-analysis: 92.9 mole% d_5 and 7.1% d_4
or 98.6 atom% D.

PARTIAL PROTONATION OF FLUOROBENZENE-d_5.

A mixture of 0.5 g of fluorobenzene and 5.0 ml of water in presence of activated platinum was heated during 3 1/2 hours at 80° C in the rocking furnace. Then the tube was quenched in ice and opened. The fluorobenzene was extracted with ether and dried over $MgSO_4$. The ether was removed on the vacuum line and a yield of 0.4 ml (81.9%) was obtained by distillation of the residue in a Späth bulb.

Mass-analysis: 55.8 mole% d_5, 33.0% d_4, 9.6% d_3, 1.6% d_2
or, 88.6 atom% D.

BENZONITRILE-d_5.

Aniline-d_7 (3 g) was diazotized as described for the preparation of chlorobenzene-d_5.

This diazonium salt was added in small portions to a solution of cuprous cyanide, prepared as described in Vogel (44), at 60-70° C on a steam bath with vigorous stirring by hand with each addition. Then a condenser was attached to the flask and the mixture heated for 15 minutes on the steam bath or until decomposition ceased. The benzonitrile formed was steam distilled, extracted with pentane, washed with 10% NaOH solution, 10% H_2SO_4 and finally water. The pentane solution was dried over $MgSO_4$ and filtered into a Späth bulb. The solvent was removed slowly on the vacuum line keeping the distilling flask immersed in ice water. The residue, with a vapor pressure of 0.5 mm, was collected in a bulb cooled in dry ice.

The benzonitrile-d_5 obtained (1.6 g, 49.5%), analyzed 100% purity by vapor phase chromatography.

Mass-analysis: 94.2 mole% d_5, 5.8% d_4 or, 98.8 atom % D.

PARTIAL PHOTONATION OF BENZONITRILE-d_5. (First run)

Benzonitrile-d_5 (0.50 g), water (5.0 ml) and platinum black were heated in a sealed tube at 110° for 6 hours in the rocking furnace. The tube was then quenched in ice and opened. The nitrile was extracted with pentane and distilled as before in a Späth bulb attached to a vacuum line.

The proton content, determined by N.M.R. spectroscopy was only 2.1 atom% D.

This product was exchanged again as above at 110° for 28 hours.

Mass-analysis: 50.1 mole% d_5, 34.3 d_4, 12.0% d_3 and 3.6% d_2

or, 86.1 atom% D.

PARTIAL PROTONATION OF BENZONITRILE-d_5.(Second run)

The mixture of benzonitrile, water and platinum black was heated at 110° for 24 hours and purified as in the first run.

Mass-analysis: 81.5 mole% d_5, 17.0% d_4 and 1.5% d_3

or, 96.0 atom% D.

PARTIAL PROTONATION OF ANILINE-d_7.

Aniline-d_7 (1.o g), water (10.0 ml) and platinum black in a sealed tube were heated at 73° C for 7 minutes in a rocking furnace without shaking and for 3 minutes with shaking. Then the tube was quenched in ice, opened and the aniline extracted with pentane, dried over $MgSO_4$ and distilled on a vacuum line in a Späth bulb. The yield was 0.8 g (80%).

As the mass-analysis could not be done on the aniline, it was converted to the chlorobenzene and analyzed.

Mass-analysis: 55.8 mole% d_5, 29.6% d_4, 13.0% d_3, 1.6% d_2 or 87.9 atom% D.

N,N-DIMETHYLANILINE-d_5.

Aniline-d_7 (1.4 g) and freshly distilled methyl phosphate (b.p. 194°C) (1.4 g) were placed in a 25 ml round bottom flask equipped with a reflux condenser protected from moisture by a Drierite tube. The mixture was heated to a boil for 2 hours, then cooled to 50° C. A solution of 1.2 g of NaOD in 5 ml of D_2O was added and the mixture was refluxed for 1.5 hours, then cooled to 40° C and transferred to a separatory funnel with pentane. The lower layer was drained off rapidly. The pentane solution was dried over $MgSO_4$ and filtered into a Späth bulb. The pentane was removed under reduced pressure and the low vapor pressure residue was distilled into one of the bulbs cooled in dry ice.

The material (1.4 g, 79.5%) was analyzed by vapor phase chromatography and found to be 98% pure. The small amount of impurity was N-methylaniline.

Unfortunately this compound could not be analyzed by mass-spectrometry since a methylene cation was formed readily and by abstraction of a deuterium atom gave erroneous results.

According to N.M.R. spectroscopy, the product analyzed 3.4 atom% H, (1.70% ortho, 0.82% meta, 0.85% para).

PARTIAL PROTONATION OF N,N-DIMETHYLANILINE-d_5.

N,N-Dimethylaniline-d_5 (0.50 g) was exchanged with water (5.0 ml) in presence of platinum black for 4 hours at 80° C in the rocking furnace. Then the tube was quenched in ice and opened. The N,N-dimethylaniline was purified by extraction in pentane and distillation in a Spȧth bulb on a vacuum line.

The product was analyzed for the proton content by N.M.R. spectroscopy and was found to be 1.87% ortho, 2.50% meta, 2.94% para or 7.3 atom% H.

PHENOL-d_6.

Phenol (10 g) was exchanged with heavy water (50 ml) in presence of platinum black in a sealed tube at 130° C for 24 hours in a rocking furnace. Then the phenol was extracted with ether. The ether was removed under reduced pressure and the phenol exchanged again. The procedure was repeated four times before a phenol analyzing 99 atom% D by N.M.R. spectroscopy was obtained. The overall yield was 9 g (90%).

Phenol-d_6 could not be analyzed by mass-spectrometry for the same reason as mentioned for aniline-d_7. The analysis was therefore done on anisole-d_5 prepared from this phenol. Methylation is known to occur without any exchange of the deuterium on the ring (42).

ANISOLE-d_5.

Clean sodium (0.26 g) was added to deuterium oxide (5 ml) in a 25 ml 2-necked round bottom flask equipped with a separatory funnel, a magnetic stirring bar and a reflux condenser protected from moisture by a Drierite tube.

To this alkaline solution was added 1 g of deuterated phenol. The solution was cooled in an ice bath and dimethyl sulphate(1.34 g) was added during a period of 20 minutes. The mixture was stirred vigorously by means of a magnetic stirrer for 2 hours in the cold and under reflux for 1/2 hour. It was then cooled in ice water, extracted with ether, washed successively with water, 10% H_2SO_4 and twice with water. The ether solution was dried over $MgSO_4$ and filtered into a Späth bulb. The ether was removed under reduced pressure. The anisole-d_5 which weighed 0.6 g (53.1%) was collected in one of the bulbs kept in dry ice and analyzed 99.7% pure by V.P.C.

Mass-analysis: 97.5 mole% d_5, 2.5% d_4

or, 99.5 atom% D.

PARTIAL PROTONATION OF ANISOLE-d_5.

Anisole-d_5 (0.50 g) was protonated during 6 hours at 100° C in a sealed tube with 5.0 ml of water in presence of platinum black. Then the tube was quenched in ice water and 0.39 g (78%) of anisole, purified by distillation in a Späth bulb, was obtained.

Mass-analysis: 65.2 mole% d_5, 28.5% d_4, 5.4% d_3, 0.9% d_2

or, 91.6 atom% D.

PARTIAL PROTONATION OF PHENOL-d_6.

Phenol-d_6 (0.50 g) was exchanged with water (5.0 ml) in presence of platinum black at 78° C for 2 hours. Then, 0.41 g (82%) of phenol was obtained by distillation in a Späth bulb.

The deuterated phenol obtained was converted to anisole whose mass-analysis was as follows: 66.3 mole% d_5, 17.8% d_4, 9.5% d_3, 4.6% d_2, 1.8% d_1, or, 88.4 atom% D.

PHENETOLE-d_5.

The phenetole-d_5 was prepared by the same procedure as for anisole-d_5 using diethyl sulphate instead of dimethyl sulphate. The product which analyzed 100% pure by V.P.C. was obtained in 74.2% yield (0.91 g).

Mass-analysis: 97.8 mole% d_5 and 2.2% d_4,
or, 99.6 atom% D.

PARTIAL PROTONATION OF PHENETOLE-d_5.

Phenetole-d_5 (0.50 g) was partially protonated with water (5.0 ml) in presence of platinum for 13 hours at 120° C and was purified as described for anisole-d_5. The yield of distillate was 0.45 g (90%).

Mass-analysis: 53.9 mole% d_5, 35.1% d_4, 9.4% d_3 and 1.6% d_2
or, 88.3 atom% D.

PHENOL (92% deuterated).

Phenol (3.5 g, 11.16 mmole) was exchanged for 3 days at 130° C in a sealed tube with 25 ml of deuterium oxide (137.50 mmole) in presence of 0.1 g of activated platinum.

The product was worked up as described for phenol-d_6.

ANISOLE and PHENETOLE (92% deuterated).

Anisole and phenetole (92% deuterated) were prepared as described for the preparation of anisole-d_5 and phenetole-d_5.

The products analyzed 92 atom% D by N.M.R. spectroscopy.

PARTIAL PROTONATION OF ANISOLE AND PHENETOLE (92% deuterated).

Deuterated anisole and phenetole were partially protonated as described for the partial protonation of anisole-d_5 and phenetole-d_5.

The proton content of the products were determined by N.M.R. spectroscopy and analyzed as follow:

29.5 atom% H for anisole and 22.8 atom% H for phenetole.

BENZOIC-d_5 ACID.

Benzoic-d_5 acid was prepared by two methods. The first consisted of exchanging potassium benzoate with deuterium oxide in the presence of platinum black. Unfortunately, after four exchanges there still remained 4.5 atom% proton on the ring mostly in the 2 and 6 positions. Since accurate calculation was complicated in a compound not uniformly deuterated, it was decided to prepare the benzoic-d_5 acid through another method.

BENZENE-d_6.

Benzene (25 ml) was exchanged four times with deuterium oxide (50 ml) in presence of platinum black for 24 hours at 130° C in a sealed tube.

Mass-analysis: 93.8 mole% d_6 and 6.2% d_5
or 99.0 atom% D.

BROMOBENZENE-d_5.

Bromobenzene-d_5 was prepared according to the method developed by Best and Wilson (45).

Bromine (53 g) and mercuric oxide (160 g) were added alternately, each in 10 separate portions to water (530 ml) with shaking, which was continued for 10 minutes after the addition was complete. The solution was then filtered. The filtrate, together with hexadeuteriobenzene (8 g) was shaken in a stoppered bottle for 16 hours. The lower layer was separated and dissolved in pentane, and the pentane solution was shaken with sodium carbonate solution, dried over $MgSO_4$ and distilled at atmospheric pressure.

The fraction boiling at 154-155° C was collected separately (9.2 g. 59.8%) and analyzed 99.3% pure by V.P.C.

Mass-analysis: 95.2 mole% d_5 and 4.8% d_4
or, 99.0 atom% D.

BENZOIC-d_5 ACID.

To magnesium turnings (1.4 g) and 10 ml of ether (dried over Na) in a 200 ml 3-necked round bottom flask equipped with a separatory funnel, a gas inlet tube for dry Argon and a reflux condenser protected from moisture with a Drierite tube, a crystal of iodine was added and the mixture was stirred by means of a magnetic stirrer until the solution decolorized. Then, bromobenzene-d_5 (9.2 g) in 50 ml of dry ether was added dropwise. Dry Argon was passed slowly through the apparatus during the reaction. The agitation was continued for 1/2 hour after the addition. Dry CO_2 gas was then introduced through the gas inlet, while keeping the reaction medium in cold water, until reaction ceased. The complex was hydrolyzed with diluted hydrochloric acid and the aqueous layer discarded. The ether solution was dried over $MgSO_4$ and filtered into a sublimation apparatus. The ether was removed under reduced pressure and the remaining solid was sublimed.

The sublimate was dissolved in 10% solution of KOH and the solution was washed twice with pentane and then neutralized with concentrated hydrochloric acid. The solid that separated was filtered and dried in air. The yield was 3.8 g (52.7%), m.p. 122° C (uncorrected).

METHYL BENZOATE-d_5.

To a solution of benzoic-d_5 acid (1.5 g) in 5 ml of ether was added an ethereal solution of diazomethane until the yellow color of diazomethane persisted. The excess of diazomethane and ether was removed by distillation and the residue was distilled in a Späth bulb under reduced pressure. The distillate (1.6 g, 96.3%) analyzed 100% pure by V.P.C.

Mass-analysis: 95 Mole% d_5, 5% d_4, or, 99 atom% D.

PARTIAL PROTONATION OF METHYL BENZOATE-d_5.

Methyl benzoate-d_5 (0.50 g) was exchanged with 5.0 ml of water in presence of platinum black for 2 hours at 80° C. The methyl benzoate was extracted with ether and distilled in a Späth bulb on a vacuum line in a yield of 0.45 g (90%).

Mass-analysis: 88.2 mole% d_5, 9.8 d_4, 2.0% d_3
or, 97.2 atom% D.

ACETOPHENONE-d_5.

Mg turnings (0.88 g) were placed in a 100 ml 3-necked flask equipped with a magnetic stirring bar, two gas inlets and a reflux condenser protected from moisture with a Drierite tube. After the air had been displaced by Argon, dry ether and a crystal of iodine were added. After the color of iodine had disappeared, methyl bromide gas was added to the reaction mixture at such a rate that the ether boiled gently. When all the Mg had disappeared, the gas flow was stopped. Then the solution was cooled in ice and anhydrous $CdCl_2$ (3.6 g) (freshly dried at 100° C in an oven) was added all at once. The mixture was heated to a boil while stirring for 40 minutes. A finely divided powder was formed. To the flask was attached a twelve-inch Vigreux column fixed to a still head. The ether was distilled very fast on the steam bath until the distillation started to slow down. Then dry benzene (35 ml) was added through a funnel and the distillation was continued until the temperature reached 70° C. The flask was then attached to the original condenser and heated nearly to boil. Benzoyl-d_5 chloride, prepared from 1.5 g of benzoic-d_5 acid and 3.5 ml of thionyl chloride, in dry benzene was added. The stirring and heating were continued for 3 minutes after the addition. Then the mixture was hydrolyzed with a solution of 10% ammonium chloride. The organic layer was separated in a separatory funnel, washed with water, dried over $MgSO_4$ and filtered. The benzene was removed under reduced pressure on a vacuum line. The residue was transferred into a Späth bulb and distilled under reduced pressure at room temperature. The fraction having a vapor pressure of 0.5 mm was collected in one of the bulbs kept in dry ice in a yield of 0.53 g (36%).

The vapor phase chromatographic analysis on the product showed that it was 96% pure. It contained 4 impurities of the order of approximately 1% each.

The acetophenone analyzed 99 atom% D by N.M.R. spectroscopy.

PARTIAL PROTONATION OF ACETOPHENONE-d_5.

Acetophenone-d_5 (0.50 g) was exchanged with water (5.0 ml) in presence of platinum black for 6 hours at 100° C in a sealed tube.

The product of the exchange reaction (0.4 g, 80%) was analyzed by N.M.R. spectroscopy and no noticeable increase in hydrogen content was observed.

This product was exchanged again as above at 100° C for 7.5 hours and a very small increase in hydrogen in the ring could be detected. No detectable quantity of phenyl methyl carbinol was found by vapor phase chromatography.

The relative intensities of the N.M.R. peaks were measured by weight and were as follows: 3.9 mg for ortho, 6.3 mg for meta and 4.4 mg for para protons.

These figures are approximative and not too dependable. But they coincide with the relative figures obtained for the other compounds.

PARTIAL PROTONATION OF BROMOBENZENE-d_5.

Bromobenzene-d_5 (0.5 g) was exchanged at 148° C for 5 days in a sealed tube with water (4 g) in presence of 10 mg of activated Adam's catalyst. Then the tube was cooled in ice water and opened. The bromobenzene was taken in pentane, dried over $MgSO_4$ and filtered in a Smith bulb. The pentane was removed on a vacuum line while keeping the solution in ice. The bromobenzene was collected in one of the bulbs kept in dry ice.

It was found that the water at the end of the exchange reaction was acidic (pH = 2).

Mass-analysis: 92.8 mole% d_5, 7.2% d_4 or 98.5 atom% D.

ANTHRACENE-d_{10}.

The anthracene-d_{10} was obtained from Merck, Sharp and Dohme of Canada.

M.p. 218.5-219.5° C (uncorrected)

Mass-analysis: 84.2 mole% d_{10}, 14.4 % d_9, 1.4% d_8
or, 98.3 atom% D.

PARTIAL PROTONATION OF ANTHRACENE-d_{10}.

Anthracene-d_{10} (0.5 g) was exchanged with water (5.0 ml) in the presence of platinum black at 210° C for 4 hours in a sealed tube shaken in the rocking furnace. This high temperature was needed in order to obtain an exchange reaction since at 200° C for 2 hours, practically no exchange was observed.

The product of the reaction was filtered and sublimed.

Mass-analysis:	57.80 mole%	d_{10}
	10.00	d_9
	1.26	d_8
	0.86	d_7
	1.46	d_6
	2.35	d_5
	3.49	d_4
	5.62	d_3
	11.18	d_2
	4.61	d_1
	1.36	d_0

or, 76.24 atom% D.

N.M.R. analysis: The protonation between the α, β and 9-10 positions was in a ratio of 1 to 1 to 0.

NAPHTHALENE-d_8

Naphthalene-d_8 was obtained from Merck, Sharp and Dohme of Canada.

Mass-analysis: 93.1 mole% d_8, 6.9% d_7

or, 99.1 atom% D.

PARTIAL PROTONATION OF NAPHTHALENE-d_8.

Naphthalene-d_8, (0.25 g) was exchanged with water (2.5 ml) in presence of 6.2 mg of activated platinum in a sealed tube at 85° for 20 minutes with shaking in the rocking furnace. Then the tube was quenched in ice and opened. The naphthalene was taken up in ether and filtered into a sublimation apparatus. The ether was removed under reduced pressure and the dry residue sublimed at 0.1 mm pressure at 40° C. A yield of 0.22 g (88%) was obtained.

Mass-analysis:	33.7 mole%	d_8
	28.0	d_7
	16.4	d_6
	9.0	d_5
	5.2	d_4
	3.2	d_3
	2.2	d_2
	1.6	d_1
	0.9	d_0

or, 80.6 atom% D.

N.M.R. analysis: The protonation between the α and the β positions was in a ratio of 1 to 2.

PARTIAL DEUTERATION OF POTASSIUM p-METHOXYBENZOATE.

Potassium p-methoxybenzoate (2.2 g) was exchanged with D_2O (25 ml) (pH = 8) in presence of platinum black (50 mg) at 140° C for 66 hours in a sealed glass tubing agitated by a rocking furnace. Then the tube was cooled in ice and opened. The catalyst was filtered off and the filtrate pumped to dryness under reduced pressure at 70° C. The solid residue was dissolved in 25 ml of water and acidified with 15% HCl. The resulting p-methoxybenzoic acid was filtered and washed with 50 ml of water and finally dried in air overnight. The yield was 1.4 g (75.7%) m.p. 184-185° C.

METHYL p-METHOXYBENZOATE (partially deuterated).

The partially deuterated p-methoxybenzoic acid (0.5 g) was esterified with an excess of diazomethane in ether. Then the excess diazomethane and most of the ether were removed on the vacuum line. The remaining solution was washed with 10% KOH, followed by water, dried over $MgSO_4$ and filtered by gravity into a Späth bulb. The rest of the ether was removed under reduced pressure and the product was collected in a bulb cooled in dry ice.

Mass-analysis: 12.4 mole% d_0, 32.2% d_1, 33.1% d_2, 17.1% d_3,
5.2% d_4, or 42.6 atom% D.

N.M.R. spectroscopic analysis showed that 32 atom% D was introduced in the 2 and 6 positions, and 55.5 atom% D in the 3 and 5 positions.

Calculated M value: 1.15.

PARTIAL DEUTERATION OF POTASSIUM p-CHLOROBENZOATE.

Potassium p-chlorobenzoate (2.16 g) was exchanged with D_2O (25 ml) (pH = 8) in presence of platinum black (50 mg) at 140° C for 66 hours in a sealed tube. Then the product was converted to p-chlorobenzoic acid as described for potassium p-methoxybenzoate. The yield obtained was 1.4 g (80.4%); m.p. 242.5-243° C.

METHYL p-CHLOROBENZOATE (partially deuterated).

The partially deuterated p-chlorobenzoic acid (0.5 g) obtained above, was esterified with diazomethane, washed with 10% KOH solution and finally water. The ether solution was dried with $MgSO_4$ and the ether removed on the vacuum line. The methyl p-chlorobenzoate was distilled in a Späth bulb.

Mass-analysis: 48.7 mole% d_0, 33.5% d_1, 14.4% d_2, 3.4% d_3
or 18.0 atom% D.

N.M.R. spectroscopic analysis showed that 18 atom% D was introduced in the 2 and 6 positions, and 18 atom% D in the 3 and 5 positions.

Calculated M value: 1.10.

RESULTS AND DISCUSSION

Careful control of the various factors, namely, the activity of the catalyst, the agitation of the reaction mixture, the temperature, the concentration and purity of the deuterated starting materials, ensured the constancy of the results. The most important factor seemed to be the activity of the catalyst. As the M value decreases with a decrease in activity of the catalyst (46, 37), the platinum was activated in such a manner that the M values were very close to unity (Table III) in order to minimize any ambiguity in the results due to multiple exchange. This objective was achieved with most of the compounds but in the cases of aniline, phenol, anthracene and naphthalene, the M values were greater than 1.

Calculation of the M value.

From equations 7 and 9:

$$M = \frac{k_\phi}{k_b} = \frac{\phi_\infty}{100-b_\infty} \; \frac{\log \dfrac{(\phi_\infty)}{(\phi_\infty-\phi)}}{\log \dfrac{(100-b_\infty)}{(b-b_\infty)}}$$

where ϕ_∞ = 390 for potassium p-methoxybenzoate and potassium p-chlorobenzoate,

= 480 for monosubstituted benzenes,

= 770 for anthracene and naphthalene.

b_∞ = 0 due to the high concentration of water.

Example:

For anisole,

MASS SPECTROMETRIC ANALYSIS OF PARTIAL PROTONATED DEUTERIO-MONOSUBSTITUTED BENZENES.

Compound	Mole% D						Atom%	F	Atom% D of
	d_5	d_4	d_3	d_2	d_1	d_0	D	Value	starting material
Fluorobenzene	55.8	33.0	9.6	1.6	0	0	88.6	1.00	98.6
Chlorobenzene	54.5	34.4	9.5	1.6	0	0	88.3	1.01	98.8
Anisole	65.2	28.5	5.4	0.9	0	0	91.6	1.01	99.5
Phenetole	53.9	35.1	9.4	1.6	0	0	88.3	1.01	99.6
Benzonitrile	50.1	34.3	12.0	3.6	0	0	86.1	1.08	98.8
Methyl benzoate	88.2	9.8	2.0	0	0	0	97.2	1.05	99.0
Aniline	55.8	29.6	13.0	1.6	0	0	87.9	1.11	98.8
Phenol	66.3	17.8	9.5	4.6	1.8	0	88.4	1.49	99.5
Bromobenzene	92.8	7.2	0	0	0	0	98.5		99.0

TABLE III

MASS SPECTROMETRIC ANALYSIS

Compound	Mole% D											Atom% D	M value
	d_{10}	d_9	d_8	d_7	d_6	d_5	d_4	d_3	d_2	d_1	d_0		
Anthracene	57.8 (84.2)	10.0 (14.4)	1.26 (1.4)	0.86	1.46	2.35	3.49	5.62	11.18	4.61	1.36	76.24 (98.3)	3.54
Naphthalene			33.7 (93.1)	28.0 (6.9)	16.4	9.0	5.2	3.2	2.2	1.6	0.9	80.6 (99.1)	1.6

The number in parenthesis is the mass-analysis of the starting material.

TABLE III (Cont'd)

$$M = \frac{480}{100} \quad \frac{\log \frac{480}{480-42}}{\log \frac{100}{65.2}} = 1.01$$

The accuracy of the M value depends on many factors, but most of these are negligible and, very often, cancelled each other. The most important are:

a) The accuracy of the ϕ_∞ value.
With compounds having non-equivalent hydrogen in the ring, it would be difficult to obtain this value accurately, but as it is very high under the present experimental conditions, the error is very small.

b) The value b_∞.
This value was estimated to be zero even though in mono-substituted benzenes only the deuterium in three positions is exchanging. The proton content at the calculated equilibrium being close to 96 atom% D, then the b_∞ value is necessarily very close to zero.

c) The accuracy of the mass-spectrometric results.
The isotopic effect in mass-analysis has already been estimated to be negligible.

d) The non-equivalence of the protons on the ring.
This is the most important factor which could introduce an appreciable error in the M value. The magnitude of this effect, experimentally or theoretically, is not known, but it should not be very much greater than ±0.03.

e) Correction for residual protons in starting compounds.

This is important for anthracene and naphthalene but negligible for the other compounds studied.

The mass-spectrometric data reported in table III are based on the assumption that the isotopic effect is negligible, i.e. the difference in the probability of ionization of C_6D_5X in comparison with C_6D_4HX and $C_6D_3H_2X$, where X is the substituent, was insignificant but, for higher protonation, a small correction would have been necessary according to Meyerson (41).

The net amount of protons introduced in the ring was calculated by subtracting the proton content of the starting material from the proton content of the protonated product. In the cases of deuterated aniline and phenol, the mass-analyses were done on chlorobenzene and anisole respectively and for N,N-dimethylaniline and acetophenone, the deuterium determination was done by N.M.R. spectroscopy, since no accurate mass-analyses were possible for these compounds.

The relative percentage of protons introduced in ortho, meta and para positions was determined by N.M.R. spectroscopic analyses. The results obtained are tabulated in table IV. As only a small quantity of protons was added for most of the compounds, identification of the bands was relatively simple since, by deuterium decoupling of the protons, the bands, which were separated by at least three c.p.s. for most of the compounds studied, were well resolved at high deuteration (Table V). For anisole and phenetole, however, it was not as simple since the chemical shifts of the ortho and para protons were very close and were not easily identified.

N.M.R. SPECTROSCOPIC ANALYSIS.

Compound		Distribution of Aromatic Protons			Atom% H
		ortho	meta	para	
Fluorobenzene	A	1.99	6.27	3.14	11.4
	B	0.56	0.56	0.28	1.4
Chlorobenzene	A	0.41	7.08	4.21	11.7
	B	0.48	0.48	0.24	1.2
Anisole	A	0.20	4.05	4.05	8.3
	B	0.20	0.20	0.10	0.5
Phenetole	A	0.20	5.50	6.00	11.7
	B	0.20	0.20	0.10	0.5
Benzonitrile	A	1.68	5.76	6.42	13.9
	B	0.48	0.48	0.24	1.2
Methyl benzoate	A	0.51	1.17	1.14	2.8
	B	0.40	0.40	0.20	1.0
Aniline	A	10.48	0.94	0.70	12.1
	B	0.48	0.48	0.24	1.2
Phenol	A	8.50	2.32	0.77	11.6
	B	0.20	0.20	0.10	0.5
N,N-Dimethylaniline	A	1.87	2.50	2.94	7.3
	B	1.70	0.82	0.88	3.4
Bromobenzene	No detectable exchange				

A - the partial protonated material B - the starting material

TABLE IV

CHEMICAL SHIFTS

(relative to internal benzene in cps)

Compound	ortho	meta	para	Solvent and concentration (w/v)	Previous ref.
Phenol	33	11	28	10% CCl_4	30
Fluorobenzene	17.5	2.5	14.0	5% C_6H_{12}	47
Chlorobenzene	-0.85	4.86	7.95	5% C_6H_{12}	47
Aniline	47.5	12	34	50% CCl_4	47
Anisole	26.9	5.0	25.1	3% C_6H_{12}	47
Phenetole	27.5	5.9	25.9	10% C_6H_{12}	
N,N-Dimethylaniline	34	-2.7	26	neat	47
Benzonitrile	-16.1	-6.2	-13.2	10% C_6H_{12}	
Methyl benzoate	-44.8	-3.0	-9.1	10% C_6H_{12}	30
Acetophenone	-37	-5.5	-12	50% C_6H_{12}	

TABLE V

In order to clarify this matter, anisole and phenetole deuterated to approximately 92% with a ratio of 2:2:1 in ortho, meta and para positions respectively, were prepared by deuteration of phenol with a known quantity of D_2O in presence of platinum catalyst in order to obtain 92% deuteration at equilibrium. The chemical shifts of the ortho and para protons were then easily determined. When these compounds were partially protonated, the band due to the para proton was increasing at a faster rate than the one for the ortho protons for both compounds i.e. the para position in anisole and phenetole was exchanging at a faster rate than in the ortho positions.

The chemical shifts obtained were in very close agreement with those reported by Tiers (30), Schneider (47) and Corio (48). The difference in chemical shifts between the ortho and the para protons in N,N-dimethylaniline is reported to be only 0.9 cps in 15% colution in cyclohexane, but when the analysis was done on the neat compound a separation of 8 cps was observed. The chemical shifts of protons in the ortho, meta and para positions of phenetole, benzonitrile and acetophenone are reported for the first time in table V.

From the results obtained by mass-spectrometric analyses (Table III) and N.M.R. spectroscopic measurements (Table IV), it was possible to calculate the relative rates (Table VI) for the ortho, meta and para positions in the monosubstituted benzenes.

The relative rates of reaction at the ortho, meta and para positions were obtained by subtracting the residual amount of protons in the starting material from the amount present in each position of the partially protonated product.

PARTIAL RATE FACTORS

Compound	ortho	meta	para	A value (49,50)
Phenol	6.2	1.6	1.0	0.7-1.25
Fluorobenzene	0.25	1.0	1.0	0.25
Chlorobenzene	0	0.83	1.0	0.4-0.5
Aniline	11	0.5±0.2	1.0	1.1-1.7
Anisole	0	0.49	1.0	0.7
Phenetole	0	0.45	1.0	1.0
Benzonitrile	0.10±0.03	0.43	1.0	0.15-0.25
Methyl benzoate	0.05±0.03	0.41	1.0	0.7-1.5
N,N-Dimethylaniline	0.04	0.41	1.0	2.1
Acetophenone*	0	0.3±0.1	1.0	

* Not accurate values due to very small introduction of protons.

TABLE VI

Example:

The relative rates for the exchange of deuterated anisole.

a) Anisole-d_5 (99.5 atom% D) has 0.1% residual proton in each position, as determined by mass-spectrometry and N.M.R. spectroscopy (Tables III and IV).

b) The percentage of protons in each position after exchange was 0.20% ortho, 4.05% meta and 4.05% para.

c) The net amount of hydrogen introduced is then 0% in ortho, 3.85% in meta and 3.95% in para positions.

d) Then the relative rates for anisole are: (Table VI)

ortho	0
meta	0.49
para	1.0

The relative rates for the meta position decreased in the following order:

$OH > F > Cl > NH_2 > OCH_3 > OCH_2CH_3 > CN = CO_2CH_3 > N(CH_3)_2 > COCH_3 > Br$

The large extent of protonation in the ortho positions of phenol and aniline may depend on their large H values. Much smaller ortho protonation was noticed in fluorobenzene, benzonitrile, methyl benzoate and N,N-dimethylaniline, and none in other cases.

Table VII shows that the overall rate of exchange of the monosubstituted benzenes decreased approximately in the following order:

$NH_2 > OH > F > OCH_3 > Cl > OCH_2CH_3 > CO_2CH_3 = CN > N(CH_3)_2 > COCH_3 > Br$

OVERALL RATE OF EXCHANGE

Compound	T°C	Time hrs.	Atom% D sm	Atom% D ppm	Atom% H fm
Aniline	73	3 min.	98.8	87.9	10.9
Phenol	78	2	99.5	88.4	10.1
Fluorobenzene	80	3.5	98.8	88.6	10.2
Anisole	100	6	99.5	91.2	8.3
Chlorobenzene	110	18	98.8	88.3	10.5
Phenetole	120	13	99.6	88.7	10.9
Methyl benzoate	80	7	99.0	96.8	2.2
Benzonitrile	110	24	98.9	96.0	2.9
N,N-Dimethylaniline	100	6	96.2	94.3	1.9
Acetophenone	120	24	≈99.0	≈98.0	≈1.0
Bromobenzene	148	5 days	99.0	98.5	0.5

TABLE VII

sm = starting material

ppm = partial protonation material

fm = final material

A close relation between the overall rate of exchange of the ring deuterium and the relative rates for the meta position in the series of compounds studied was observed. The only exceptions were phenol, aniline and chlorobenzene. The high M values for phenol and aniline can explain this behavior but this is not the case for chlorobenzene. It was noticed that the aqueous layer became very slightly acidic during the partial protonation of chlorobenzene-d_5 and a positive test for chloride ions was obtained with silver nitrate in dilute nitric acid solution. The decomposition was more serious in the case of bromobenzene. An acidic medium was surely responsible for the lowering of the rate of exchange reaction in both cases. No actual relation between the solubility of the monosubstituted benzenes and their rate of exchange reactions could be made.

Finally, partial protonations on naphthalene-d_8 and phenanthrene-d_{10}, and partial deuteration on the potassium salts of p-chloro and p-methoxy benzoic acids at a pH of 8 were done in order to study the orientation effect in molecules possessing more sterically hindered positions.

The proton distribution in the partial protonation of naphthalene-d_8 was found to be in a ratio of 1 to 2 in the α and β positions with a M value of approximately 1.6. For phenanthrene, no preference was noticed between the α and the β positions. This can be explained by a very high amount of anthracene-d_2 in the product and a large M value, 3.54.

A ratio of deuteration of 3 to 5 was found for the 2 and 3 positions respectively in potassium p-methoxy benzoate with a M value of 1.15, but for potassium p-chlorobenzoate the ratio was nearly equalled with a M value of 1.10. Since the M values are low for both compounds the reaction must occur through a simple exchange mechanism. Furthermore, this conclusion is corroborated by the fact that there was a difference in the rates of deuteration in the 2 and 3 positions of potassium p-chlorobenzoate.

Several things seem obvious from the results obtained. The most important one is the large ortho steric effect in heterogeneous platinum exchange reactions. The effect was reported in the literature several times, especially by Garnett (31, 51) for alkylated benzenes and a few monosubstituted benzenes, but not quantitatively since they were working with exchange reactions carried nearly to equilibrium. The relative ortho effect reported in table VI is very significant for most of the compounds studied with only two serious exceptions, namely phenol and aniline which have higher M values, probably because exchange is proceeding by another mechanism. The relative rates observed for the meta position followed approximately the same order as the A values* for most of the compounds studied with only one serious exception, benzonitrile. The most logical explanation for the behavior of benzonitrile is that the linearly cylindrical nitrile group affects sterically the catalytic exchange reaction more seriously than the A value would indicate, because the steric effect in the transition state leading to meta exchange is much larger than the steric effect due to neighboring axial protons in the 3 and 5 positions. (See diagram 20).

Another observation in support of the large importance of the steric effect is the resemblance between the relative meta rates and the

* "A value" is the free-energy difference between the equatorial-axial conformation of the particular monosubstituted cyclohexane. These values provide information about the order of steric interactions of substituents in organic molecules.

overall rate of exchange of the compounds studied. The only other significant exception besides phenol and aniline, which are proceeding through a different mechanism, is chlorobenzene. The detection of a small amount of chloride ions in the aqueous medium of the partial protonation reaction could be the reason for a reduction in the overall rate of the exchange reaction. A much greater rate reducing effect was also observed for partial protonation of bromobenzene, for which a pH of 2 was obtained due probably to the presence of hydrobromic acid formed during the reaction. The results obtained by Garnett (6) that the ortho positions in bromobenzene were exchanging faster than the ortho positions in chlorobenzene could be explained since the acidity of the medium was greater for bromobenzene than for chlorobenzene and the reaction occurred through an electrophilic mechanism.

(20)

The second obvious characteristic of the heterogeneous platinum exchange reaction is the lack of observable electronic effect. This effect was also observed by Garnett (31) when he failed to observe any difference in orientation during deuteration of the benzene rings in toluene and ααα-trifluorotoluene. Since he was working at very high deuteration, nearly at equilibrium, a relatively small electronic effect could certainly not be observed. The results shown on table VI prove without any doubt that the electronic effect is not participating in platinum catalyzed exchange reactions since the meta partial rate factors are independent of the electronic nature of any type of substituents.

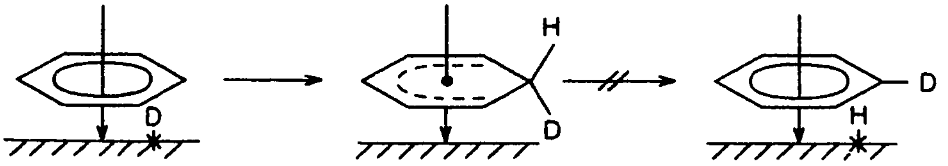
The lack of ortho steric effect in aniline and phenol is most likely due to strong chemisorption of the catalyst on the substituents which would orient the aromatic molecules in such a way as to expose the ortho positions to a facile exchange reaction. This exchange may thus be considered to proceed through another mechanism than the one for the other positions on the ring, or for other compounds.

The steric effect for anthracene and naphthalene could not be studied since their M values were much too large for there to be any significance in the data.

The relative importance of the two possible mechanisms of heterogeneous platinum deuterium exchange reactions, namely the associative and the dissociative mechanisms, for olefinic and aromatic compounds is an interesting subject for discussion. As the main object of this thesis is to bring some further evidence for one or the other mechanism, an attempt will be made to present objections and supports for each of them in the light of the results obtained.

π-Complex formation may have importance in the associative mechanism since this step could be rate determining, but in the dissociative mechanism, it is certainly not rate determining and no proof can be given of its importance in aromatic catalytic exchange reactions when $M=1$. However, if $M>1$ then it can explain the multiple exchange reaction.

The main objection to the associative mechanism is that there is no obvious mechanism for removal of the hydrogen in the transition state since the platinum is chemisorbed flat on the surface of the benzene ring on the opposite side of the hydrogen attached to a sp^3 hybridized carbon. No free rotation is allowed (Eq. 21) since the π-adsorption bond cannot be broken.



(21)

The dissociative mechanism implies that no hydrogen is needed for the exchange reaction. But, it is well known that nitrobenzene (4), diphenylacetylene (52), and acetophenone, do not exchange and this seems to be related to the deactivation of the catalyst through a fast reduction of the substituents by the chemisorbed hydrogen on the surface of the catalyst. The deactivation of the catalyst in boiling water is another example of the importance of the concentration of hydrogen on the surface of the catalyst to the rate of the exchange reaction. It seems possible that the exchange reaction might occur without chemisorbed hydrogen on the catalyst but the reaction should then be very slow.

The possibility of the multiple exchange mechanism by chemisorption of the catalyst on adjacent carbons is eliminated since the amount of deuterium introduced in potassium p-methoxybenzoate was not the same in the 2 and 3 positions and also the M value is too low for this mechanism.

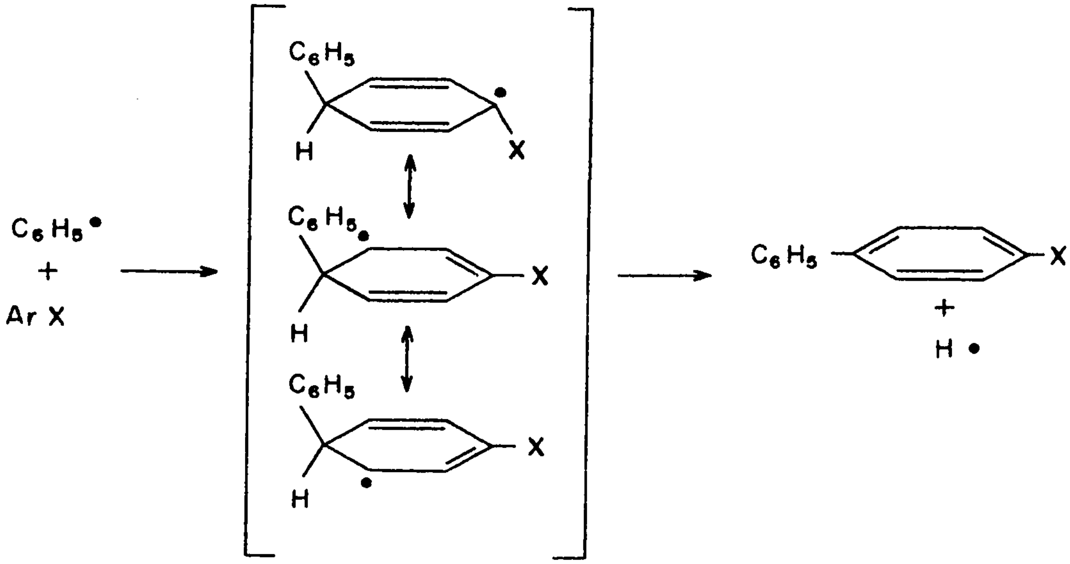
The exchange proceeds through a one point adsorption and the stability of this complex determines the extent of the exchange at every adsorption.

The associative mechanism is supported by the importance of the presence of hydrogen.

The great importance of steric effects in the reaction is certainly in agreement with the dissociative mechanism even though this effect could also be important in the associative mechanism since the chemisorption of the catalyst as a π-complex should not be centered on the ring in monosubstituted benzenes but should be closer to the para and meta positions due to steric interaction of the substituent. The considerable deactivation of the overall rate of exchange for benzonitrile and acetophenone is most likely due to the deactivation of the catalyst by slow reduction of the substituent even though no trace of reduced products could be detected by V.P.C. analysis.

Therefore, the objections and the supports to the associative and the dissociative mechanisms as presented by Rooney and Garnett are controversial and the evidence given for or against these mechanisms is not convincing.

The formation of an adsorbed phenyl radical as presented by Kemball (19) as an intermediate in the catalytic exchange reaction is in agreement with the intermediate formed when a phenyl radical attacks a monosubstituted benzene (Eq. 22).



(22)

DeTar (53) gave good supporting evidence for this mechanism when he isolated the very reactive 1-4 dihydrobiphenyl compound. No biphenyl was detected in the products of the reaction.

The relative reactivity of the various positions on a given aromatic ring toward free-radical aromatic substitution was determined by Hey (54) and listed in Augood's review (55). Even though the determination of the ortho, meta and para substitution products does not give a very reliable indication of the relative rate, it has some significance when compared with the results reported in table VI. Unfortunately only a few benzenes bearing the same substituents as those we report on have been studied and their relative activity for the meta and para positions are shown in table VIII.

PARTIAL RATE FACTOR.

	meta	para
Fluorobenzene	1.25	1
Chlorobenzene	0.90	1
Benzonitrile	0.2	1

TABLE VIII

The most important effect to note is that there is little, if any, electronic effect of the substituent on the relative rates of meta and para attack.

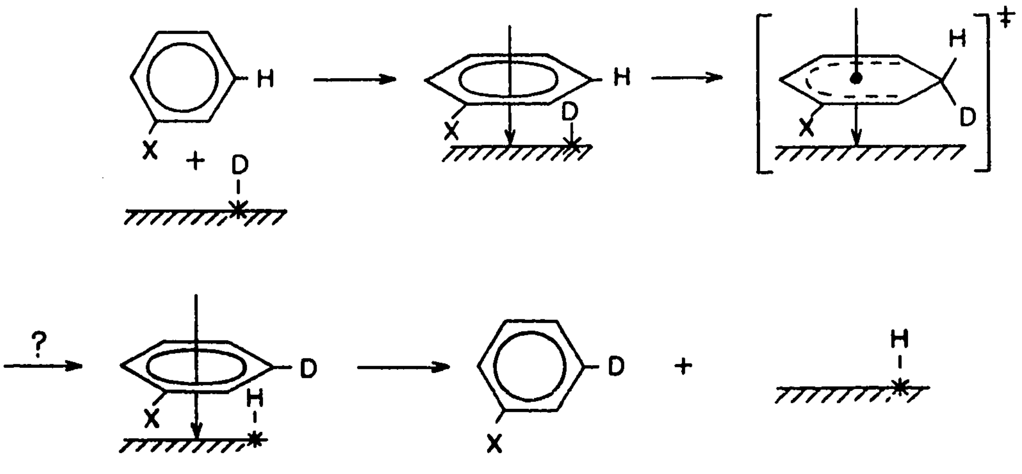
With all these data, the transition state for the platinum catalyzed exchange reaction of monosubstituted benzenes can be written as shown in equations 23 and 24 for the two mechanisms proposed.

There are two important differences to note:

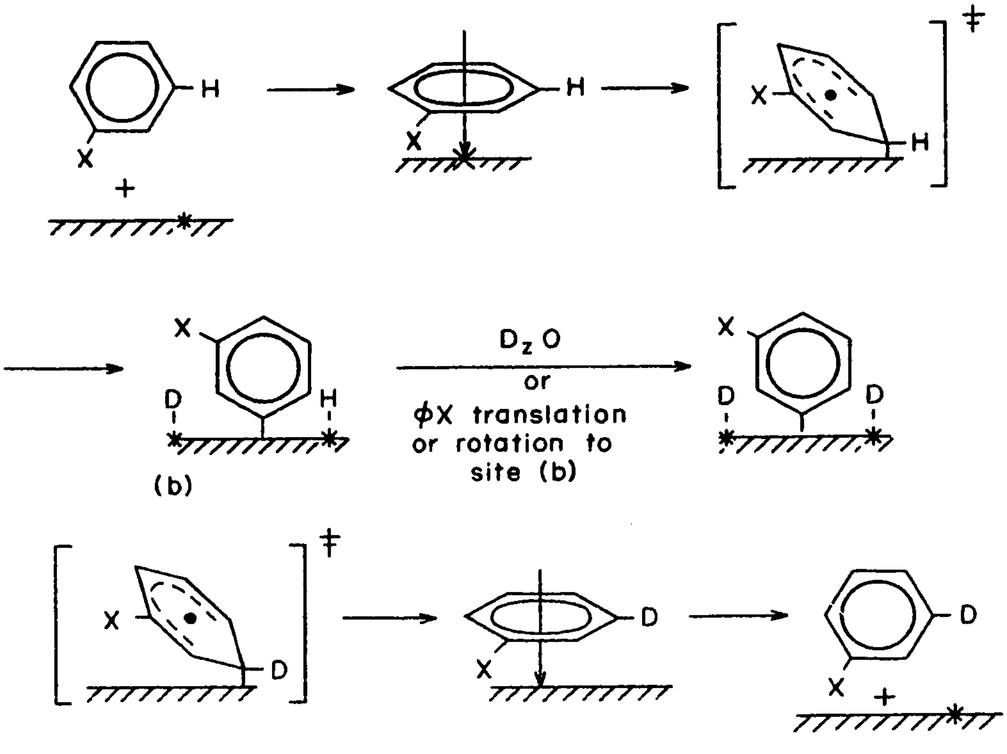
a) In the dissociative mechanism, the π-complex formation, while likely, is not necessary when M = 1, whereas in the associative mechanism it is required as a π-allylic complex in order to bind the intermediate to the surface of the catalyst.

b) In the dissociative mechanism, the meta substituent is located much closer to the catalyst surface since a M-C bond is being formed. It is therefore clear that the dissociative mechanism should be more sensitive to the steric effect of a substituent in the meta position. The steric effect of an ortho substituent is still larger.

Thus the associative mechanism is less likely to exhibit the



Associative Mechanism
Equation 23



Dissociative Mechanism
Equation 24

Note: the dot represents a delocalized unpaired electron.

observed steric effects. Also it fails to provide a reasonable mechanism for removal of the hydrogen in the transition state. For these reasons the results obtained will be discussed on the assumption that the dissociative mechanism is the most important in the reaction.

The main controversy for this mechanism is the non-importance of the presence of hydrogen for an exchange reaction to occur, according to Garnett, on one hand, and the great reduction in rate of exchange reaction when the concentration of hydrogen is reduced, on the other hand. This can be explained if it is accepted that the rate determining step is the reaction of chemisorbed deuterium or hydrogen on the surface of the catalyst with the σ-bonded metal complex. Then the concentration of chemisorbed deuterium should affect the rate of the exchange reaction. This effect was noticeable when the catalyst was treated with boiling water prior to the exchange reaction. The non-reactivity of nitrobenzene, diphenylacetylene and acetophenone can be explained by the relatively faster reduction reaction of the substituents at the expense of the reaction of the chemisorbed deuterium with the σ-bonded metal intermediate. An additional point worth emphasis is that it is quite possible that the decrease in rate with decrease in available chemisorbed hydrogen is due to a change in the catalyst itself.

The evidence for the dissociative mechanism, proposed by Garnett without any good quantitative experimental facts, can be summarized under the following headings.

1. The large ortho steric effect. (Table VI).

For most of the compounds studied, the steric effect due to the substituent prevents a direct approach of the catalyst on the ortho positions.

2. The relative rates in the meta position. (Table VI).
   The catalyst has to approach the molecule at the least hindered site.
3. Different mechanisms for reduction and exchange reactions.
   Kemball's finding that the exchange reaction has to occur through a different mechanism than for the reduction reaction is respected by the dissociative mechanism. The reduction is most likely happening through an associative mechanism.
4. The transition state.
   The geometric configuration of the transition state places the proton of the sp^3 hybridized carbon in a good position for its abstraction by the π-complex adsorbed catalyst.

Other factors which are equally compatible with either the dissociative mechanism or the associative mechanism are summarized below.

1. The non-electrical participation.
   The deuteration of the meta and the para positions depends only on the steric hindrance of the substituent and not on its electronic directing influence.
2. The multiple exchange reaction.
   The multiple exchange reaction depends on the activity of the catalyst to form a π-complex with the benzene ring. The stability of this complex relative to the energy of the T.S. for exchange determines the multiplicity of the exchange reaction.

3. The concentration of deuterium chemisorbed on the catalyst. The exchange reaction can occur without deuterium chemisorbed on the catalyst but the reaction will be very slow. Then the greater the concentration of chemisorbed deuterium on the catalyst, the faster the exchange reaction.

CONCLUSIONS.

The mechanism of heterogeneous exchange reactions presented by many workers are subjected to many objections simply because they were based on general qualitative data and not enough relation was made between one result and the other. More attention had to be given to the complex in the transition state and the behavior of the chemisorbed hydrogen on the catalyst. This is a very sensitive field since a mechanism of reaction which can be considered to be appropriate under certain conditions may not be so under others. The nature and the physical form of the catalyst may have its primordial importance.

The chemisorbed phenyl radical in heterogeneous exchange reaction on platinum catalyst seems to agree with the mechanism of free-radical reaction. The quantitative results obtained in this thesis are not in contradiction with the dissociative mechanism which was proposed by Garnett. The presence of chemisorbed hydrogen on the catalyst explained the relative rate of the exchange reaction.

The evidence given is far from being absolute and a need for further theoretical and experimental work is necessary for a clearer picture of the mechanism of heterogeneous exchange reaction.

CLAIMS FOR ORIGINAL WORK.

1. The relative rates of ortho, meta and para substitution in heterogeneous catalytic exchange reactions for monosubstituted benzenes have been calculated.
2. The chemical shifts of a few monosubstituted benzenes have been determined.
3. Quantitative experimental facts in favor of the dissociative mechanism.

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