The Steric Effect in the Platinum-Catalyzed Exchange Reaction between Aromatic Ring Protons and Deuterium Oxide

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Abstract: The relative rates of the platinum-catalyzed exchange of heavy water with the *ortho*, *meta*, and *para* protons in several monosubstituted benzenes have been determined. A very large steric effect but no detectable electronic effect was observed. These results are interpreted as support for the dissociative mechanism of exchange.

The substitution of deuterium for hydrogen by the reaction of aromatic compounds with heavy water in the presence of a platinum catalyst is an important method for introducing deuterium into the aromatic ring.[1] The mechanism by which the reaction proceeds has been investigated extensively by Garnett and his co-workers.[2] The various aspects which have been studied include the effect of substituents on the over-all reactivity,[2a-c] the effect of substituents on the positional reactivity,[2d-f] the effect of catalyst preparation on the rate of exchange,[2g-i] a comparison of the rate of randomization between benzene and benzene-d_6 with the rate of exchange of benzene,[2j] and the efficacy of various amines and heterocyclic compounds as poisons.[2k-n] Garnett has considered two likely mechanisms by which the exchange might occur (see Figure 1). These are both modifications of the mechanisms originally proposed by Farkas and Farkas and by Horiuti and Polanyi.[3] Both mechanisms involve initial adsorption of benzene on the catalyst surface as a π complex. The major distinction is that the associative mechanism, A, involves a direct substitution of chemisorbed deuterium for hydrogen, whereas the dissociative mechanism, B, requires a replacement of hydrogen by platinum to give a chemisorbed phenyl radical. This subsequently suffers displacement by chemisorbed deuterium to give the exchanged product. Garnett concluded from his studies that exchange occurs *via* the dissociative π-complex mechanism. In order to evaluate this conclusion, we will summarize briefly the most pertinent of this data.

First of all, he observed an inverse relation between the efficiency of various poisons and their ionization potential which he offered as evidence for π-complex formation.[2k,m] The change in reactivity within a series of alkylbenzenes was also investigated.[2a] It was found that reactivity decreased in the following order: benzene, ethylbenzene, *o*-xylene, cumene, toluene, benzotrifluoride, *m*-xylene, *p*-xylene, hemimellitine, *t*-butylbenzene, mesitylene. It was also stated that no exchange *ortho* to the substituent occurred in *t*-butylbenzene, benzotrifluoride, and mesitylene, nor in the 2 position of *m*-xylene. Unfortunately, little detail of analytical methods was given, so that the accuracy of this work cannot be assessed. The author concluded that two steric effects were operative: (a) π-complex inhibition, (b) inhibition of formation of the platinum–carbon bond. The former determined substrate reactivity, the latter the orientation effect. The only report of an examination of the relative reactivity of the three ring positions in a monosubstituted benzene was a qualitative study of the exchange of chloro- and bromobenzene[2e] (*vide infra*). The most probing test of mechanism was the determination of the rate of randomization of deuterium between C_6H_6 and C_6D_6 in the presence of platinum catalyst.[2j] The fact that randomization did occur was cited as compelling evidence for the dissociative mechanism since this mechanism does not require the presence of hydrogen on the catalyst, whereas the associative mechanism does. That randomization occurred at almost the same rate as exchange between benzene and heavy water using the same catalyst, was cited as proof that the dissociative mechanism was operative in both reactions. Again an assessment of their conclusion is hampered by a lack of specific knowledge of catalyst composition. To validate their conclusion, they must provide evidence that the catalyst surface was free of adsorbed hydrogen.[4] This is doubtful in view of the work of Plisken and Eischens.[5] They studied the infrared spectrum of deuterium and hydrogen chemisorbed on platinum which was supported on γ-alumina. Two types of platinum–hydrogen bonds were indicated by the presence of two bands attributed to adsorbed hydrogen. Although the exact nature of binding could not be

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(1) L. C. Leitch, *Can. J. Chem.*, **32**, 813 (1954).

(2) (a) J. L. Garnett and W. A. Sollich, *J. Catalysis*, **2**, 350 (1963); (b) W. G. Brown and J. L. Garnett, *J. Am. Chem. Soc.*, **80**, 5272 (1958); (c) J. L. Garnett and W. A. Sollich, *Nature*, **201**, 902 (1964); (d) J. L. Garnett, D. J. Henderson, W. A. Sollich, and G. V. D. Tiers, *Tetrahedron Letters*, **15**, 516 (1961); (e) J. L. Garnett and W. A. Sollich, *Australian J. Chem.*, **14**, 441 (1961); (f) J. L. Garnett, *Nucleonics*, **20**, No. 12, 86 (1962); (g) J. L. Garnett and W. A. Sollich, *J. Catalysis*, **2**, 339 (1963); (h) G. E. Calf and J. L. Garnett, *J. Phys. Chem.*, **68**, 3887 (1964); (i) J. L. Garnett and W. A. Sollich, *ibid.*, **68**, 436 (1964); (j) J. L. Garnett and W. A. Sollich-Baumgartner, *ibid.*, **68**, 3177 (1964); (k) J. L. Garnett and W. A. Sollich, *Australian J. Chem.*, **15**, 56 (1962); (l) G. E. Calf and J. L. Garnett, *J. Catalysis*, **3**, 461 (1964); (m) R. A. Ashby and J. L. Garnett, *Australian J. Chem.*, **16**, 549 (1963); (n) J. L. Garnett and W. A. Sollich-Baumgartner, *ibid.*, **18**, 993 (1965).

(3) For a comprehensive review of the early work on the mechanisms of exchange and hydrogenation see: T. I. Taylor, "Catalysis," Vol. V, Reinhold Publishing Corp., New York, N. Y., 1957, p 257.

(4) Previously, the same type of argument resulted in a great deal of controversy regarding the mechanism of exchange of olefinic and acetylenic hydrocarbons. Conflicting results from the laboratories of different workers made it obvious that rigorous conclusions were not possible, ref 3, p 320.

(5) W. A. Plisken and R. P. Eischens, *Z. Physik. Chem.* (Frankfurt), **24**, 11 (1960).

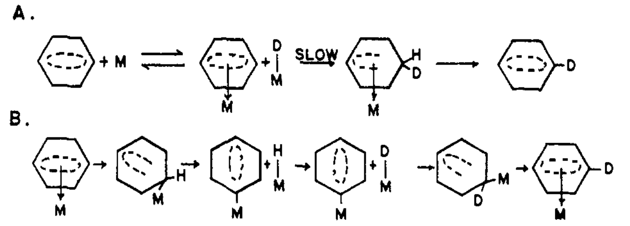

Figure 1. Possible mechanisms of deuterium exchange; A = associative, B = dissociative.

proven, it was found that one type of adsorbed hydrogen remained on the surface after evacuation at 10^{-4} mm and 35° for 10 min. Garnett's standard procedure involves sealing off the catalyst at room temperature and 0.06 mm pressure![2g] A further criticism of Garnett's conclusion is his reliance on the comparison of rates for two reactions in different solvents.[6]

Recently Hirota and Ueda have reported on the isomerism and self-exchange of *m*-deuteriotoluene on platinum black,[7] and on the isotopic exchange of *p*-xylene with heavy water using several transition metal catalysts including platinum.[8] These authors interpret the results of exchange in terms of a dissociative mechanism. The observed isomerism of *m*-deuteriotoluene to *p*-deuteriotoluene on platinum was postulated to occur *via* the σ-diadsorbed intermediate shown in Figure 2.

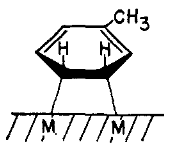

Figure 2. Toluene, σ-diadsorbed on platinum.

In view of the lack of any quantitative data on the exchange reaction, we have determined the relative rates of isotopic substitution in the *ortho*, *meta*, and *para* positions of a variety of monosubstituted benzenes. We have done this in the following way. By standard labeling techniques (see Experimental Section for details), each benzene derivative was deuterated to greater than 98.5 atom % in the ring positions (analysis by low voltage mass spectrometry). The distribution of the residual protons was determined by nmr spectral analysis and in all cases the *ortho*:*meta*:*para* ratios were statistical, *i.e.*, 2:2:1. The deuterated compound was then treated with ordinary water in the presence of platinum catalyst under conditions which introduced between 5 and 15 atom % hydrogen (by mass spectral analysis). The distribution of protons was again determined by quantitative nmr analysis. By subtraction, the atom % protons introduced into each of the *ortho*, *meta*, and *para* positions was calculated. Since the extent of protonation was small, we can equate the increase in proton content at the *ortho*, *meta*, and *para* positions to their relative rates of exchange. The above approach was used in order to take advantage of the technique of "massive deuteration".[2d,9] In this way the nmr absorption of protonated product is due to protons whose vicinal substituents are mainly deuterium atoms. The effect of H–D coupling, although small, was completely removed by spin–decoupling.[10] In most cases the assignment of specific peaks to the individual ring protons was unambiguous, thanks to the previous work of Spiesecke and Schneider.[11] Phenetole gave peaks whose chemical shifts were almost identical with those of anisole so in this case assignments were made by analogy. In the spectrum of 99% deuterated benzonitrile (10% w/v in cyclohexane) we observed sharp peaks at −16.1, −13.2, and −6.2 cps from the internal standard, benzene. The intensity ratios were 2:1:2, respectively, which indicated that the peak at −13.2 cps was due to *para* protons. The *meta* protons were previously assigned a chemical shift of −10.5 cps (1% w/v in cyclohexane).[12] It seemed likely that the peak at −6.2 cps in our sample was due to *meta*-proton absorption. This was confirmed by the spectrum of partially protonated product which showed in addition to the three single peaks, a weak AB pattern (ν_A = −6.2, ν_B = −13.0, J_{AB} = 8.0 cps) due to diprotonated material. The magnitude of *J* requires the protons to be vicinal and since ν_B is due to *para* absorption, ν_A must be the *meta* absorption. Assignments for methyl benzoate were made in an analogous way. Table I gives the chemical shifts of the compounds under the conditions we employed for our measurements. There are small deviations from the previously reported values,[11,12] which undoubtedly arise from the greater concentration of solute used in our spectral determinations.[13] They are not large enough to affect the reliability of peak assignments. However the near coincidence of *ortho* and *para* proton absorption in anisole and phenetole did create a problem. Protonation of 99% deuterated material gave a compound whose spectrum showed only two aromatic absorption peaks. The peak due to the *para* protons was obscuring the relatively small *ortho* absorption (or *vice*

Table I. Chemical Shifts of Aromatic Protons[a]

Compound	*ortho*	*meta*	*para*	% concn and solvent	Previous reference
Phenol	33	11	28	10, CCl_4	2d
Fluorobenzene	17.5	2.5	14.0	5, C_6H_{12}	11
Chlorobenzene	−0.9	4.9	7.9	5, C_6H_{12}	11
Aniline	47.5	12	34	50, CCl_4	11
Anisole	26.9	5.0	25.1	3, C_6H_{12}	11
Phenetole	27.5	5.9	25.9	10, C_6H_{12}	
N,N-Dimethylaniline	34	−2.7	26	Neat	11
Benzonitrile	−16.1	−6.2	−13.2	10, C_6H_{12}	12
Methyl benzoate	−44.8	−3.0	−9.1	10, C_6H_{12}	12

[a] Cps at 60 Mcps from internal benzene.

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(6) Reference 3, p 266 provides evidence that solvent effects are important.

(7) K. Hirota and T. Ueda, *Tetrahedron Letters*, 2351 (1965).

(8) K. Hirota and T. Ueda, Proceedings of the Third International Congress on Catalysis, 1238 (1965).

(9) G. V. D. Tiers, *J. Chem. Phys.*, **29**, 963 (1958).

(10) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p 229.

(11) H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, **35**, 731 (1961).

(12) F. Laugenbucher, E. D. Schmid, and R. Mecke, *ibid.*, **39**, 1901 (1963).

(13) The possibility of an isotope effect on the chemical shift was ruled out since the chemical shifts of the *para* protons in monoprotonated and vicinal diprotonated compounds were identical within the experimental error of measurement.

Table II. Mass Spectrometric Analysis of Partially Protonated Products

Compound	Mole % D d_5	d_4	d_3	d_2	d_1	d_0	Atom % D	M value	Atom % D of starting M
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[a]	55.8	29.6	13.0	1.6	0	0	87.9	1.11	98.8
Phenol[b]	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

[a] Converted to chlorobenzene, then analyzed. [b] Converted to anisole, then analyzed.

versa). That substitution had taken place *para* to the ether substituent was established in separate experiments. A sample of randomly deuterated anisole (92 atom % D) was prepared by carrying out one exchange reaction until equilibrium was attained. This material was then treated briefly with water and platinum so that only a few atom % of hydrogen was incorporated. The spectrum of this product showed all three of the aromatic protons and clearly indicated from peak intensities that protonation had occurred in the *meta* and *para* positions. A duplicate experiment on phenetole gave the same results.

The mass spectral and nmr analyses of the reprotonated compounds are given in Tables II and III.

Table III. Nmr Spectroscopic Analysis

Compound		Distribution of aromatic protons *ortho*	*meta*	*para*	Atom % H
Fluorobenzene	A[a]	1.99	6.27	3.14	11.4
	B[a]	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

[a] A = the partially protonated material; B = the starting material.

From the distribution of mono-, di-, and trisubstituted products in Table II it is possible to determine whether the protonation had occurred in a stepwise or multiple reaction. The proportion of multiple substitution is calculated as an M value, where $M = k_\phi/k_b$ and k_ϕ is essentially the rate of appearance of product and k_b is rate of disappearance of starting material. These are calculated according to the method of Kemball.[14] When $M = 1$, only a single exchange is occurring for each adsorption of the aromatic compound on the catalyst surface, when $M = 2$, two protons exchange per adsorption. With only two significant exceptions, the M values for exchange of the compounds in Table II were equal to 1.0 within the limits of experimental error[15] (the catalyst had been prepared purposefully to provide this desired activity).

For reactions in which $M = 1$, we can rule out exchange by a mechanism involving *cis* addition of hydrogen, desorption to form cyclohexadiene, readsorption of cyclohexadiene on the other side of the molecule and *cis* elimination to give a product which has exchanged two adjacent hydrogens for deuterium. As a cross-check on the validity of this interpretation of M values, the compound potassium *p*-methoxybenzoate was deuterated and the distribution of protons determined by nmr. The exchange was found to be 1.6 times faster *meta* to the carboxylate group than *ortho* to it. Thus a stepwise mechanism must be operative since a *cis* addition, *cis* elimination mechanism would give rise to equal rates of exchange in the two aromatic positions.

From the data in Table II and the quantitative nmr analysis, the relative rates of exchange in the three ring positions were calculated, the results of which are given in Table IV. For each compound, the rate of substitution in the *ortho* and *meta* positions is expressed relative to the rate at the *para* position which is set equal to 1. One can immediately see the marked interference to *ortho* substitution, which is exhibited by all substituents except fluorine, amino, and hydroxyl. We will defer discussion of the latter two cases which

Table IV. Partial Rate Factors

Compound	*ortho*	*meta*	*para*	A value[a]
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	0.06 ± 0.03	0.41	1.0	0.7–1.5
N,N-Dimethylaniline	0.04	0.41	1.0	2.1

[a] See ref 17.

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(14) C. Kemball, *Advan. Catalysis*, 11, 223 (1959).

(15) There are several assumptions implicit in the calculation of M.[14] In our case it was necessary to assume equal reactivity in the *meta* and *para* positions and no reactivity in the *ortho* positions. Since the extent of reaction is small, the error introduced should be negligible.

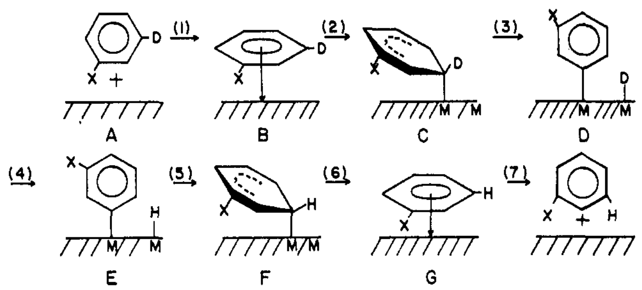

Figure 3. Detailed mechanism of deuterium exchange at the *meta* position of a monosubstituted benzene.

likely represent a subtle change in mechanism. Since the fluorine atom is only slightly larger than hydrogen, its steric effect ought to be small.[16] In most other compounds the rate of substitution in an *ortho* position is less than one-eightieth of the rate at the *para* position. Of course the *ortho*-substitution rates though immeasurably small may be finite. The only literature example with which our results can be compared is the aforementioned deuteration of chloro- and bromobenzene.[2e] Under Garnett's reaction conditions, chlorobenzene exchanged 16% in the *ortho* and completely elsewhere in the ring; bromobenzene exchanged 20% in the *ortho* and completely elsewhere (analyses were by infrared). From this data he dismissed the steric effect as being insignificant. It is obvious that any steric effects were masked by allowing the reaction to proceed too close to the random distribution of deuterium. In our hands bromobenzene exchange was very slow. It was noticed that after exchange the reaction medium was acidic. It is possible that bromide ion, produced by hydrogenolysis was acting as a poison. The data in any event would be doubtful since exchange could also occur *via* an electrophilic pathway.

The data in Table IV also show that the relative rate of *meta* substitution is subject to an appreciable steric effect. To illustrate the correlation of rate with the size of the substituent, the *A* value[17] of each substiuent is also given in Table IV. With the exception of the nitrile group, the relative rate of *meta* substitution decreases as the *A* value increases. The failure of nitrile to correlate is most likely a reflection of its geometry. The C≡N group encounters less unfavorable interaction when axially oriented on a cyclohexane ring than during *meta* exchange. The length of the group is likely responsible for the latter effect, whereas the van der Waals radius of the carbon atom is most important in determining the *A* value.[18] It is also apparent from the results in Table IV that the electronic character of the substituent does not determine the position of exchange (compare F *vs.* H, OCH_3 *vs.* CN). Garnett also noted the lack of electronic effect on the position of exchange, since both benzotrifluoride and *t*-butylbenzene exhibited "*ortho* deactivation."[2a]

There are some features of the data which may be considered surprising or inconsistent. A small but definite amount of *ortho* substitution occurred in the exchange of benzonitrile and methyl benzoate. This is most likely occurring *via* a second pathway with $M = 2$, which, according to the *M* values in Table II, contributes 8 and 5%, respectively, to the over-all reaction. Still larger *M* values were observed for phenol and aniline.

In accordance with the above observations we wish to outline the most likely mechanism. This is depicted in Figure 3, illustrating reaction at the *meta* position during protonation of the deuterated compound. This is basically the dissociative mechanism of Garnett. The steps are given in somewhat greater detail as we wish to comment on the evidence pertaining to each of them.

Step 1. When $M = 1$ there is no direct proof for the formation of the π complex, B. If π-complex formation does occur, it is certainly not the slow step in the reaction. As *M* becomes larger, it is likely because of the change from step 3 to step 7 as the slow step.

Step 2. This depicts the formation of a σ complex, a metal-bound cyclohexadienyl radical similar to that proposed for the homolytic substitution of benzene by phenyl radicals. Although homolytic reactions show some susceptibility to the electronic effect of subsituents, the effect is slight compared with ionic reactions.[19] Such an intermediate as C is therefore consistent with the lack of an electronic substituent effect.

Step 3. Here a platinum–carbon σ bond is formed.[20] This is likely the slow step when $M = 1$, since Garnett observed an isotope effect $k_D/k_T = 1.7$.[2j] Because the stability of C will, in all likelihood, determine the energy barrier for this step, it will be C that determines both the orientation effect and reactivity of our compounds. We are not able to obtain accurate total rate constants from our experiments. We can, however, estimate the relative reactivity of each compound from the reaction time, temperature, and extent of protonation. This leads to the following approximate order of over-all reactivity; $NH_2 > OH > F > OCH_3 > Cl > OCH_2CH_3 > COOCH_3 \approx CN > N(CH_3)_2 > Br$. It can be seen generally, that the over-all rate decreases as the selectivity increases. This is the normal behavior exhibited by electrophilic aromatic substitutions[21] and is consistent with step 3 being the slow step. In contrast, for reactions where *M* is significantly greater than 1, the selectivity relationship would no longer hold since either π-complex formation or desorption would determine the rate while σ-complex stability would determine the orientation. Such a situation has been observed in electrophilic substitutions with nitronium fluoborate.[22] It is obvious then that Garnett's classifi-

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[16] The van der Waals radii for F and H are 1.35 and 1.2 A, respectively; see L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1945. The C–F bond length in fluorobenzene is 1.33 A compared to the C–H bond length of 1.08 A in benzene, "Tables of Interatomic Distances," The Chemical Society, London, Supplement, 1965.

[17] The *A* value is the difference in free energy between the axial and equatorial orientation of the substituent in the two chair conformations of cyclohexane. The values are quoted from E. L. Eliel, *Angew. Chem.*, 77, 787 (1965).

[18] The near equality of the A values for C≡N and C≡C—H supports this idea. The A values for C≡N are reported to be 0.15 kcal/mole, B. Rickborn and F. R. Jensen, *J. Org. Chem.*, **27**, 4606 (1962); and 0.25 kcal/mole, N. L. Allinger and W. Szkrybalto, *J. Org. Chem.*, 27, 4601 (1962). For the ethynyl group the *A* value is 0.18 kcal/mole, R. J. Ouellette, *J. Am. Chem. Soc.*, **86**, 3089 (1964).

[19] The maximum variation in relative reactivity towards phenyl radicals is shown by nitrobenzene, 8, and benzonitrile, 5, compared with benzene equal to 1. In contrast, halogenation of toluene is 1000 times faster than benzene, see: J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

[20] Evidence in support of this species is discussed by G. C. Bond, "Catalysis by Metals," Academic Press Inc., New York, N. Y., 1962, p 312. Alternative adsorption types are reviewed by G. C. Bond and P. B. Wells, *Advan. Catalysis*, **15**, 101 (1964).

[21] L. M. Stock and H. C. Brown, *J. Am. Chem. Soc.*, 81, 3323, 5621 (1959).

cation of steric effects into two types, *i.e.*, π-complex and σ-complex interaction can only be operative where π-complex formation is the *slow step.* No data concerning the M values in his reactions were given.[2a]

Step 4. This is not a well-defined process. It is included to show that an adjacent isotope must be available for exchange to occur. It is not known whether the same site is used for step 5, or other adjacent sites can supply the proton or perhaps the phenyl group is capable of migration over the surface of the catalyst.[23]

Steps 5, 6, 7. These are identical with steps 1, 2, and 3 except for the isotope effect.

We have observed an appreciable steric effect by the substituent on the relative rate of *meta vs. para* substitution. This finding requires the transition state in the rate-determining step leading to *meta* substitution to be less stable than that leading to *para* substitution. Since we have considered step 3 to be the slow step, either intermediate C, or D, or a hybrid thereof will best approximate the transition state, and we have chosen C as the model for it. It can thus be seen that the substituent X in C_{meta} encounters more unfavorable steric interaction with the catalyst surface than it does in C_{para}. The dissociative mechanism is therefore consistent with our experimental observations.

The alternative associative mechanism requires that the stability of H_{para} *vs.* H_{meta} determines the relative rate of *meta* substitution (Figure 4). In both H_{para} and H_{meta} the cyclohexadienyl ring lies parallel to the surface of the catalyst. Therefore, there should be no difference in the steric environment of X in either intermediate. It could be argued that J might be a better representation of the transition state, in which the ring is not parallel to the surface. However, the ring is sufficiently remote from the catalyst in this model that it is difficult to understand how substituents like chlorine and methoxyl could affect the rate of *meta vs. para* substitution. Two additional arguments make the intermediacy of the π-allylic species H unlikely. Although palladium shows a strong tendency to form such species,[24,25] the same is not true for platinum.[26] Also the postulate of the π-complex intermediate H or J has a major shortcoming. The hydrogen and deuterium atoms attached to the sp^3 carbon atom of H or J are in different stereochemical environments. The deuterium atom lies above the plane of the ring remote from the catalyst. In such a position it is not accessible to exchange by any reasonable mechanism. This argument has been advanced previously by Kemball.[27] We therefore conclude that only the dissociative mechanism can account for the effect of substituents on the relative rates of exchange in the three positions of monosubstituted benzenes.

It is also important to mention again that there is no direct evidence on the nature of the initially adsorbed molecule which Garnett has proposed to be the π complex, B. Some adsorbed species is certainly required and becomes important kinetically when M is greater than 1, but this requirement could equally well be fulfilled by the σ-diadsorbed species in Figure 2 or one of the other alternatives given in ref 20.

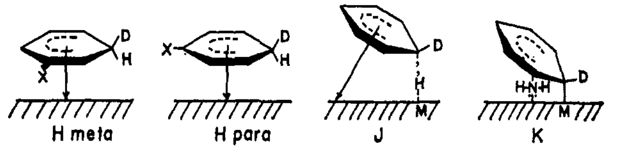

Figure 4. Intermediates in the dissociative mechanism of exchange.

The contrasting behavior of phenol and aniline should also be consistent with the dissociative mechanism. The M values indicate an increased strength of adsorption which makes desorption comparable in rate to σ-complex formation. The increased strength of adsorption likely results from an interaction of the lone pair of electrons of the substituent with the catalyst. It is this interaction which is also responsible for the large proportion of *ortho* substitution, for now C_{ortho} derives additional stabilization over C_{meta} and C_{para} (see K in Figure 4). In this connection, we should mention the results of Macdonald and Shannon.[28] They found that quinoline exchanged at positions 2, 7, and 8 in the presence of heavy water and a nickel catalyst, and that isoquinoline exchanged at positions 1 and 3 under the same conditions. From these observations, they concluded that the reaction could not be proceeding *via* the dissociative mechanism. Although the reaction involves a different catalyst, it is quite probable that a complex involving the basic nitrogen and the catalyst favors the observed exchange in much the same way that *ortho* exchange in aniline is aided. Several papers[29] involving catalysis by other transition metals of group VIII have recently appeared and while many similarities in these reactions exist we do not feel justified in extending our conclusions to other metal-catalyzed exchange reactions.

A few additional deuterated compounds were also reacted with water in the presence of platinum. The exchange of naphthalene and anthracene proceeded with M values of 1.6 and 3.5, respectively. As a result no significance could be attached to the distribution of protons in the product. Nitrobenzene and acetophenone both resist exchange.[30] Both these compounds possess reducible substituents which may have depleted the concentration of chemisorbed hydrogen which would cause a large decrease in the rate of exchange.

Experimental Section[31]

Apparatus. All exchange reactions were carried out in a homemade rocking furnace. The furnace was a metal tube whose ends were covered with screwed metal caps. Heating was achieved by a

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[22] G. Olah, S. Kuhn, S. Flood, and J. Evans, *J. Am. Chem. Soc.*, **84**, 3687 (1962).

[23] Hydrogen atoms have been shown to possess mobility when chemisorbed on the catalyst; A. Farkas and L. Farkas, *ibid.*, **60**, 22 (1938).

[24] F. G. Gault, J. J. Rooney, and C. Kemball, *J. Catalysis*, **1**, 255 (1962).

[25] J. J. Rooney, *ibid.*, **2**, 53 (1963).

[26] See G. C. Bond, ref 20, p 213.

[27] See ref 8, p 1248.

[28] C. G. Macdonald and J. J. Shannon, *Tetrahedron Letters*, **45**, 3351 (1964).

[29] C. G. Macdonald and J. J. Shannon, *Australian J. Chem.*, 18, 1009 (1965), and references therein.

[30] L. C. Leitch and R. N. Renaud, unpublished data.

[31] Vapor phase chromatograms were run on a Perkin-Elmer Model 154 instrument containing a 2-m column packed with silicone grease on diatomaceous earth (column "O"). Two instruments were employed for the mass spectrometric analyses. One was an apparatus constructed by Dr. F. P. Lossing of the National Research Council of Canada, and the second was an Hitachi Model RMU-6D. Spectra obtained from either instrument were of comparable accuracy (0.1 atom %). Analyses were done at low voltages, 7.5 to 9.0 ev in order to sup-

Table V. Summary of Experimental Conditions

Compound	Method of preparation	Conditions for partial protonation Temp, °C	Time
Aniline-d_7	From aniline, heavy water, and platinum	73	7 min
Fluorobenzene-d_5	From aniline-d_7 *via* diazonium salt	80	3.5 hr
Benzonitrile-d_5	From aniline-d_7 *via* diazonium salt	110	6 hr
N,N-Dimethylaniline-d_5	From aniline-d_7 and trimethyl phosphate	80	4 hr
Phenol-d_6	From phenol, heavy water, and platinum	78	2 hr
Anisole-d_5	From phenol-d_6 and dimethyl sulfate	100	6 hr
Phenetole-d_5	From phenol-d_6 and diethyl sulfate	120	13 hr
Bromobenzene-d_5	From bromination of benzene-d_6	148	5 days
Methyl benzoate-d_5	From bromobenzene-d_5 *via* Grignard and diazomethane	80	2 hr
Naphthalene-d_8	Merck Sharpe and Dohme, Montreal	85	20 min
Anthracene-d_{10}	Merck Sharpe and Dohme, Montreal	200	2 hr
(CH_3O)–$C_6H_4COO^-K^+$ [a]		140	66 hr

[a] This material was partially deuterated, then analyzed.

coil of metal wire wound on top of asbestos which was wrapped around the tube. Several additional layers of asbestos were then wound over the wire for insulation. The temperature inside the tube was determined by precalibration of thermometer readings *vs.* the Variac settings which controlled the current through the heating coil. The tube was fixed at the center and rocked by means of an arm connecting one end of the tube to an electric motor. The reactions were carried out in sealed glass tubes 12 cm in length, 2 cm in diameter, which were placed inside the furnace.

Catalyst. For each exchange, Adam's catalyst ($PtO_2 \cdot 2H_2O$, 12.5 mg) was placed in a pressure bottle with a pipetted volume (2.0 ml) of distilled water. The bottle was attached to an hydrogenation apparatus, evacuated to 18 mm pressure, and then activated by shaking for 10 min under 12 psi pressure of hydrogen. The resultant suspension was transferred directly to the glass tube to be used in the reaction. Experiments were also carried out using proportionately larger quantities.

Aniline-d_7. Aniline, freshly distilled (35 g), was exchanged with 50 ml of heavy water (99.7 atom % D) in the presence of activated platinum (0.1 g) in a sealed glass tube at 140° 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 Spath bulb attached to a vacuum line. A yield of 25 g (71.4%) of liquid whose vpc showed no trace of impurities was obtained.

The product was estimated to be 99 atom % D by nmr 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 was determined by mass analysis of a sample of chlorobenzene prepared from this aniline-d_7. It is known that no loss of deuterium from the aromatic ring occurs during the Sandmeyer reaction under carefully controlled conditions.[30]

Chlorobenzene-d_5. Aniline-d_7 (3.1 g) was placed in a 100-ml, round-bottomed flask equipped with a magnetic-bar stirrer, and cooled at −10° 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 sodium nitrite 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 hydrochloric acid at 0°. The cuprous chloride was prepared according to the method described in Vogel.[32] The mixture was allowed to warm up to room temperature, whereupon the solid complex decomposed. After stirring for 0.5 hr, the chlorobenzene was distilled out with steam, extracted with ether, washed with 10% sodium hydroxide solution, followed by water, dried over magnesium sulfate, 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 Spath bulb. The distillate (2.3 g, 63.2%) was found to be over 99.7% pure by vpc. Mass analysis indicated 94.2 mole % d_5 and 5.8% d_4 (98.8 atom % D).

Partial Protonation of Chlorobenzene-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 hr in the rocking furnace. The tube was cooled and opened, then the organic compound was extracted with ether, the extracts were dried over magnesium sulfate and filtered into a Späth bulb. The ether was removed slowly under reduced pressure. This was 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 indicated 54.5 mole % d_5, 34.4% d_4, 9.5% d_3, and 1.6% d_2 (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.

The above preparations are representative examples of the synthesis and exchange reactions. The preparation of the remaining deuterated compounds and the conditions used for their partial protonation are summarized in Table V.

Acknowledgment. We wish to thank the National Research Council of Canada for their generous financial support.

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press dissociation processes. The proportions of deuterated species were determined from parent peak intensities, after correcting for the C^{13} contributions of next-lower species. Since the analyses were done on compounds of low proton content the isotope effect could be neglected (see S. Meyerson, *J. Chem. Phys.*, **39**, 1445 (1963)). Nuclear magnetic resonance spectra were obtained from two instruments. A Varian A-60 Model was used for qualitative purposes. A Varian V-4302 spectrometer equipped with an NMR Specialities SD-60 spin decoupler was used for the quantitative determination of proton distributions and of the chemical shifts. Quantitative results were obtained from relative peak intensities in cases where peaks were of comparable height and well-resolved. Otherwise, areas under the curve were determined by the weighing of traces. It is difficult to assess the limits of accuracy of the nmr analyses since many variables are involved. We feel confident that any relative rate value obtained will be accurate to better than 10%, unless otherwise specified.

(32) A. I. Vogel, "Textbook of Practical Organic Chemistry," 3rd ed, Longmans Green and Co. Ltd., London, 1956, p 190.