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Platinum-Catalyzed Exchange Reactions between Normal and Deuterated Aromatics*

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Platinum-catalyzed exchange reactions between deuterated benzene and the following polycyclic aromatic hydrocarbons have been investigated: diphenyl, *ortho-*, *meta-*, and *para*-terphenyls; naphthalene; phenanthrene; pyrene, and dibenzyl. The rapid exchange of weakly adsorbed species such as diphenyl is consistent with the application of the dissociative π-complex substitution mechanism previously proposed for heavy water exchange. Aromatics which exchange slowly with deuterated benzene or heavy water were found to randomize readily (e.g., naphthalene–naphthalene-*a*-*d*). The deuteration rates of slowly exchanging species may be increased by the inclusion of strongly adsorbed reagents such as C_2H_5OD. The present results suggest that slow exchange is not due to the formation of irreversibly adsorbed poisons produced by a side reaction such as polymerization, but may be readily explained by strong, reversible π-complex adsorption.

INTRODUCTION

The difficulties associated with an interpretation of Group VIII transition-metal–catalyzed isotopic hydrogen exchange reactions between organic compounds and heavy water (or deuterium gas) in terms of the conventional associative (*1*, *2*) and dissociative (*3*) chemisorption theories have been summarized by Taylor (*4*). The problems concerning a theoretical understanding of these exchange reactions are accentuated in the deuteration of aromatic series such as the polycyclic hydrocarbons (*5*), alkylbenzenes (*6*, *7*), and heterocyclics (*5*, *8*). It has been shown that the data of these exchange experiments is more satisfactorily explained by a new mode of adsorption termed π-complex adsorption and reaction mechanisms based on this type of interaction (*6*, *9*). The possible role of π complexes in catalysis has been discussed by a number of authors (*9–14*).

Based on π-complex adsorption, two new mechanisms, namely the associative and dissociative π-complex substitution mechanisms (*5*) have been proposed for Group VIII transition-metal–catalyzed exchange between aromatics and heavy water. Evidence indicates that the latter mechanism predominates in heavy water exchange. In addition to these mechanistic implications, π-complex adsorption also satisfactorily explains the markedly different adsorption strengths observed for various aromatic compounds as measured by reagent displacement effects (*15*).

It is the purpose of the present paper to further explore the concept of π-complex adsorption by studying exchange reactions where heavy water as the source of deuterium atoms has been replaced by a deuterated organic. The system chosen is the exchange between deuterated benzene and two typical groups of aromatic compounds, e.g., the nontoxic† polyphenyls and toxic†

* Part XXII of a series entitled "Catalytic Deuterium Exchange Reactions with Organics." Part XXI, *Nature*, in press.

† Toxicity of a compound is defined by the retardation of a standard exchange reaction between benzene and water by reagent displacement effects (*7*).

polycyclics. Two explanations may be given as to why exchange reactions between two different aromatic molecules such as deuterated benzene and diphenyl may be very much slower than exchange between benzene and heavy water: (i) benzene may be displaced by the more strongly adsorbed diphenyl, or (ii) the mechanism of exchange between water and benzene may proceed predominantly by the associative rather than the dissociative π-complex substitution mechanism. This latter point is important since in the associative mechanism the presence of a second dissociatively adsorbed reagent such as water or deuterium gas is necessary to promote exchange whereas this is not required by the dissociative mechanism. Thus benzene-d_6/diphenyl exchange can only proceed via a dissociative process and so the present studies should provide further evidence to distinguish between the relative importance of the two π-complex mechanisms in catalytic exchange. It is also possible that certain aromatics are more toxic than others because of a poisoning side reaction rather than strong π-complex adsorption. This alternative explanation has been investigated by studying randomization reactions with α-monodeuterated naphthalene, naphthalene being chosen because it is the most toxic aromatic discovered to date (*7*).

Experimental

Naphthalene-α-*d* preparation. Mono-α-deuterated naphthalene was prepared from α-bromonaphthalene by the decomposition of the corresponding Grignard reagent in heavy water. The product was carefully purified by recrystallization and sublimation to remove ether and unchanged bromo derivative since both are potent catalyst poisons. The small traces of β-deuterated naphthalene formed by this method (*16*) did not interfere significantly with the measurement of the randomization rate.

Exchange reaction procedure. Exchange reactions between deuterated benzene and polycyclic aromatics were performed at 145°C in evacuated ampoules containing the reagents and hydrogen-prereduced platinum catalysts activated by methods described previously (*17*). The progress of the exchange reaction was measured by the low-voltage (~10 eV) mass spectrometric assay of benzene. The exchange rate k was calculated from the following first order rate equation:

$$-k = (2.3/t) \log \{([D]_\infty - [D]_t)/D_\infty\}$$

where $[D]_t$ and $[D]_\infty$ are the deuterium contents at time t and equilibrium, respectively.

The benzene randomization rate to which polyphenyl reactions were compared was calculated by procedures already published (*18*).

Randomization procedures. Naphthalene randomization reactions were performed in sealed, evacuated ampoules at several temperatures with prereduced hydrogen-activated platinum catalysts (*17*).

The progress of randomization was followed from changes in the infrared spectrum in the sensitive 700–900 cm^{-1} region where absorption bands are mainly due to the out-of-plane bending vibrations of five, four, three, two, and one adjacent hydrogen atoms (*19*). Spectra of products were compared to a 12.5% randomly deuterated sample. Results were subsequently confirmed by NMR measurements* of the α and β hydrogen abundances.

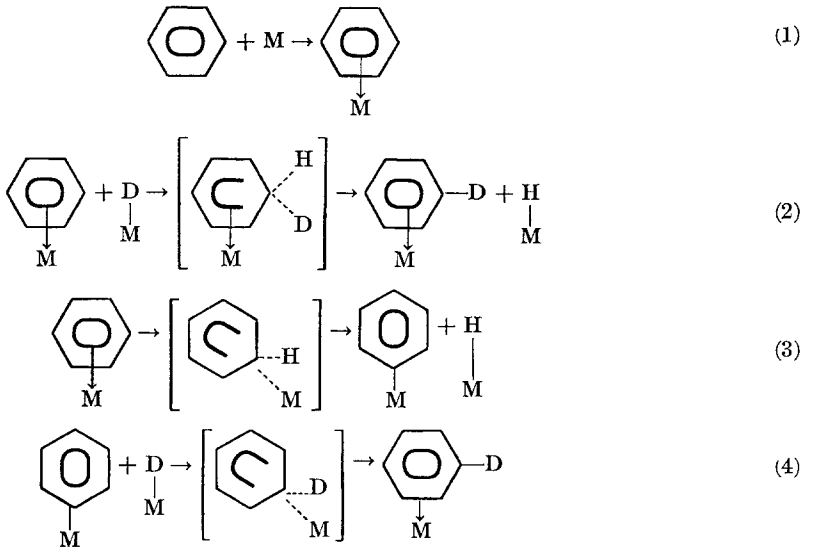
Results and Discussion

π-Complex Mechanisms

Both the associative and dissociative π-complex substitution mechanisms involve, as the first step in the reaction, bonding of the aromatic hydrocarbon to the catalyst by π-complex adsorption so that the plane of the ring is aligned parallel to the plane of the catalyst surface [Eq. (1)]. In the associative mechanism, the π-bonded aromatic undergoes a substitution reaction with a chemisorbed deuterium atom originating from the dissociative chemisorption of water [Eq. (2)]. In the dissociative mechanism the π-bonded aromatic undergoes a substitution reaction with a metal

* The authors are indebted to Dr. G. V. D. Tiers for NMR analysis of the reaction products.

radical (active site) and rotates through 90° to form a carbon–metal σ bond [Eq. (3)]. While σ bonded the molecule undergoes further rate-controlling (*18*) substitution reaction at the carbon–metal bond and returns to the π-bonded state [Eq. (4)].



It is thus clear that the essential difference between the associative and dissociative mechanisms is that only in the case of the former is it necessary to have a source of isotope from a second dissociatively adsorbed substance such as water or deuterium gas to promote exchange.

Exchange between d-Benzene and Polycyclic Aromatics

The present results confirm the importance (*18*) of the dissociative π-complex substitution mechanism by (i) the rapid exchange of deuterated benzene with the nontoxic polyphenyls (Table 1, Runs 1A–4A) and dibenzyl (Run 9B); (ii) the rapid randomization rate of normal benzene with its deuterated analog (Run 5A). Of further significance is the result that aromatics such as naphthalene, phenanthrene, and pyrene (Table 1) which were found to be toxic in both low-temperature poisoning studies and high-temperature heavy water exchange (*5, 17*) have maintained their relative toxicities in the present series of exchange reactions in the absence of heavy water.

It would thus appear that the slower exchange rates of these aromatics in the current experiments is not due to the decreased importance of the dissociative exchange mechanism but to the displacement of the less strongly adsorbed (π-complexed) benzene. The consistency in the trend of reactivities in the present series with the results of deuterium oxide exchange (*5*) provides further evidence for our previous conclusion (*17*) that the slow exchange of these compounds with deuterium oxide was not due to a toxic side reaction involving water.

In the polyphenyls, the order of reactivity (Runs 1A–4A) may be explained by steric and orbital symmetry factors governing π-complex adsorption. An increase in the number of aromatic rings decreases the ionization potential and increases the electron affinity, thus tending to strengthen π-complex adsorption. However, the favorable influence of the ionization potential and electron affinity on π-complex adsorption tends to be partly offset by (a) the decrease in orbital overlap due to steric hindrance and (b) internal cancellation as a consequence of increased nodal pattern complexity. Thus diphenyl, because of a

TABLE 1

EXCHANGE REACTIONS BETWEEN DEUTERATED BENZENE AND POLYCYCLIC AROMATICS[a]

Run	Reagents	Reagent quantities ($M \times 10^3$)	Platinum catalyst (mg)	Reaction time (hr)	$[D]_\infty$	% D in aromatic	k ($hr^{-1} \times 10^3$)
1A	Diphenyl Benzene (49.10% D)	2.34 12.8	10.6	3	37.92	47.57	4.8
2A	*o*-Terphenyl Benzene (49.10% D)	1.47 12.8	10.6	3	38.37	47.62	4.9
3A	*m*-Terphenyl Benzene (49.10% D)	1.47 12.8	10.6	3	38.37	46.70	8.3
4A	*p*-Terphenyl Benzene (49.10% D)	1.47 12.8	10.6	3	38.37	45.55	13.4
5A	Benzene Benzene (98.7% D)	12.8	10.6	3	—	—	16.4[b]
6B	Naphthalene Benzene (56% D)	6.5 17.2	37.1	24	37.3	0.35	0.039
7B	Phenanthrene Benzene (56% D)	3.08 10.1	21.8	24	37.3	0.36	0.040
8B	Pyrene Benzene (56% D)	2.46 8.27	17.9	24	37.3	0.57	0.063
9B	Dibenzyl Benzene (56% D)	2.71 9.05	19.1	24	27.3	30.2	6.6
10C	Benzene D_2O	2.06 6.18	25.2	2	50	50	—
11C	Benzene (50% D) H_2O Ethanol	1.14 1.14 1.14	59.5	17	33.4	0.0	0
12C	Naphthalene D_2O	0.60 5.05	58.9	94	73.5	1.0	0.001
13C	Naphthalene Ethanol D_2O	0.60 2.32 7.35	59.1	94	67.5	8.0	0.13

[a] Series A, B, and C were performed at 145°C with different batches of catalysts. Rate constants can therefore only be compared within each series.

[b] Randomization rate constant calculated by methods described previously (*18*).

less complex nodal pattern in bonding and antibonding orbitals, may adsorb more strongly than *p*-terphenyl, resulting in a comparatively greater displacement of benzene from the catalyst surface and a decreased reaction rate. The slower exchange of *o*- and *m*-terphenyls can be explained by deactivation of some of the ring hydrogens because of restricted rotation during carbon–metal σ-bond formation [Eq. (2)].

Randomization of Naphthalene-α-d

The purpose of the naphthalene-α-*d* randomization reactions was to show that the relatively strong toxicity of polynuclear aromatics when compared with benzene was due to stronger π-complex adsorption and not a toxic side reaction such as polymerization, which has been observed with polycyclic hydrocarbons such as azulene, anthracene, and phenanthrene.

If naphthalene poisons by covering the catalyst with a tightly adsorbed polymeric coating then normal monomeric naphthalene would be displaced and randomization could not occur. However, there should be no difficulty in the randomization reaction if strong π-complex adsorption of naphthalene is the exclusive cause of toxicity.

The preliminary aim of this investigation was to establish the feasibility of randomization. Thus Run 1 (Table 2) was performed under relatively severe experimental conditions and the results from the infrared spectra of the reaction products from this run show that extensive randomization occurred. Runs 2 and 3, performed under less severe conditions, confirm ready randomization since both reaction products gave infrared spectra identical to the product from Run 1. These conclusions were confirmed by NMR data.

When the reaction temperature is lowered from 90° to 70°C, a sudden decrease in the randomization rate is observed. This is reminiscent of similar drastic effects previously noted during the activation of catalysts for hydrogen exchange reactions, particularly in self-activation (*20*). Our present results are therefore attributed to similar factors, namely to the formation of unsuitable active sites from a reagent–catalyst interaction.

In general, the results are consistent with the interpretation that naphthalene poisons by strong, but nevertheless reversible, π-complex adsorption. This conclusion suggests that naphthalene can be deuterated more readily by reagents which adsorb more strongly than deuterium oxide. Run 11C (Table 1), demonstrates the strong adsorption properties of ethanol since it strongly poisons benzene/deuterium oxide exchange. Ethanol also possesses the following additional properties which render it suitable as a reagent for deuterium exchange reactions with strongly adsorbed aromatics: (*i*) ethanol undergoes rapid homogeneous exchange with deuterium oxide and (*ii*) ethanol exchanges rapidly with deuterium gas in the presence of platinum (*21*) and consequently with the hydrogen atoms produced from the dissociative chemisorption of naphthalene. The results of Runs 12C and 13C confirm the use of ethanol as a reagent for exchange and also the previous conclusions concerning reversible naphthalene adsorption. A similar explanation may be proposed for the beneficial effects of acetic acid in a number of deuterium (*22*) and tritium (*23*) exchange reactions since this compound also adsorbs more strongly than water (*24*).

TABLE 2
NAPHTHALENE RANDOMIZATION EXPERIMENTS

Run	Reagents	Quantity (g)	Catalyst[a] (mg)	Temperature (°C)	Time (hr)	Results: Infrared	Results: NMR β-H/α-H
1	α-*d*-Naphthalene	0.477	165	145°	240	Extensive randomization	—
2	α-*d*-Naphthalene	0.245	21.1	145°	24	Extensive randomization	1.06
3	α-*d*-Naphthalene	0.221	17.5	90°	4	Extensive randomization	1.13
4	α-*d*-Naphthalene Benzene	0.232 0.801	8.1	70°	4	No randomization	1.22

[a] A hydrogen activated (−90°C) catalyst was used in all exchange reactions.

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REFERENCES

1. HORIUTI, J., AND POLANYI, M., *Nature* **132**, 819 (1933).

2. HORIUTI, J., AND POLANYI, M., *Trans. Faraday Soc.* **30,** 1164 (1934).
3. FARKAS, A., AND FARKAS, L., *Proc. Roy. Soc. (London)* **A144,** 467 (1934).
4. TAYLOR, T. I., *in* "Catalysis" (P. H. Emmett, ed.), Vol. 5, pp. 257–400. Reinhold, New York, 1958.
5. GARNETT, J. L., AND SOLLICH, W. A., *Australian J. Chem.* **15,** 56 (1962).
6. GARNETT, J. L., AND SOLLICH, W. A., *J. Catalysis* **2,** 350 (1963).
7. GARNETT, J. L., AND SOLLICH, W. A., *J. Phys. Chem.* **69,** 1850 (1965).
8. ASHBY, R. A., AND GARNETT, J. L., *Australian J. Chem.* **16,** 549 (1963).
9. GARNETT, J. L., AND SOLLICH, W. A., *Australian J. Chem.* **14,** 441 (1961).
10. GAULT, F. G., ROONEY, J. J., AND KEMBALL, C., *J. Catalysis* **1,** 255 (1962).
11. BURWELL, R. L., JR., AND LONER, C. J., *Proc. Intern. Congr. Catalysis, 3rd, Amsterdam, 1964,* to be published (North-Holland Publ. Co., Amsterdam).
12. BOND, G. C., *in* "Catalysis by Metals," p. 313. Academic Press, London and New York, 1962.
13. VOLTER, J., *J. Catalysis* **3,** 297 (1964).
14. HIROTA, K., AND UEDA, T., *Proc. Intern. Congr. Catalysis, 3rd, Amsterdam, 1964,* to be published (North-Holland Publ. Co., Amsterdam).
15. GARNETT, J. L., AND SOLLICH-BAUMGARTNER, W. A., *Advan. Catalysis,* in press.
16. BØRGE BAK, *J. Org. Chem.* **21,** 797 (1956).
17. GARNETT, J. L., AND SOLLICH, W. A., *Australian J. Chem.* **18,** 993 (1965).
18. GARNETT, J. L., AND SOLLICH-BAUMGARTNER, W. A., *J. Phys. Chem.* **68,** 3177 (1964).
19. WERNER, R. L., KENNARD, W., AND RAYSON, D., *Australian J. Chem.* **8,** 346 (1955).
20. GARNETT, J. L., AND SOLLICH, W. A., *J. Phys. Chem.* **68,** 436 (1964).
21. MCDANIEL, E. L., AND SMITH, H. A., *Advan. Catalysis* **9,** 76 (1957).
22. ANKER, H. S., AND BLOCH, K., *J. Am. Chem. Soc.* **66,** 1752 (1944).
23. GARNETT, J. L., HENDERSON, L. J., AND SOLLICH, W. A., *Proc. Intern. Atomic Energy Agency Tritium Symp., Vienna, 1961* **2,** 47.
24. GARNETT, J. L., AND SOLLICH-BAUMGARTNER, W. A., to be published.