Mechanistic Studies of the Hydrogen Isotope Exchange Reaction Catalysed by Homogeneous Platinum Salts

By **John L. Garnett,** * **Raymond J. Hodges, Robert S. Kenyon,** and **Mervyn A. Long,** School of Chemistry, The University of New South Wales, Kensington, N.S.W., Australia 2033

Deuterium exchange between $D_2O-CH_3CO_2D$ solvent and a variety of aromatic compounds is catalysed by tetrachloroplatinate(II) ions. Rhodium and iridium salts are also shown to be homogeneous catalysts for these reactions. Multiple exchange is a consistent phenomenon of all systems. Conditions influencing the stability of platinum(II) in solution are discussed in detail and the basis for the very careful distinction between *homogeneous* catalysed exchange and the possibility of accompanying *heterogeneous* exchange by colloidal Pt^0 is delineated. The exchange kinetics with benzene show inverse first-order dependence on Cl^-. A complicated acid dependence on the reaction is found and interpreted in terms of the effect of acid on the stability of the platinum(II) in solution. These kinetic results are shown to be consistent with the predominant participation of a dissociative π-complex mechanism for the exchange process. The possible relevance of reaction intermediates proposed by other workers is also discussed.

TETRACHLOROPLATINATE(II) salts have been used extensively as catalysts in the preparation of hydrogen isotope-labelled compounds.[1-8] The conditions found most suitable for deuterium exchange involved a mixed solvent system of deuterioacetic acid and deuterium oxide. The mixed solvent permits homogeneous studies with relatively high concentrations (0.5M) of organic compounds, and the addition of traces of mineral acids, *e.g.* DCl or $DClO_4$, to this solvent enhances its acidity more than it would a pure aqueous solvent.[2] Under these conditions the catalyst does not disproportionate nor reduce to platinum(0) as readily as it does with mixtures of heavy water and organic compounds alone. In earlier work [1-4] we undertook a careful study to demonstrate unequivocally that the catalysis was due to platinum(II) in solution and not colloidal Pt^0. In this work it was shown that mineral acids such as hydrochloric acid and acetic acid stabilised the platinum(II) catalyst against reduction to the metal and the complicated acid dependence of the exchange rate on acid concentration was interpreted [2] in terms of the influence of the acid on the stability of the platinum complex. The relative reactivities of a range of substituted aromatic compounds did not follow the normal pattern of acid-catalysed exchange.

An important aspect of the homogeneous reaction is the formation of multiple deuteriated species during the initial stages of the exchange cycle for both aromatic and aliphatic compounds.[1,2,8] The kinetics show inverse chloride dependence. Thus we proposed that the mechanism of the reaction involves a fast pre-equilibrium in which a chloride ion is displaced by a solvent ligand.[9] This catalytically active intermediate subsequently reacts with the organic compound in a rate-determining step to form a charge-transfer type complex. The details of such a proposal have been published for both aliphatic and aromatic compounds.[7,9]

More recently, Gold and his co-workers [6] have published a study of the kinetics of benzene exchange using experimental conditions similar to those reported by us in our earlier work [10] and subsequently discarded in favour of an acetic acid system in which metal precipitation was minimised. These authors [6] used an exchange system containing acidified water with no acetic acid present; tritium was the source of isotope and exchange was said to be catalysed by tetrachloroplatinate(II) ions at 50 °C. These tritium experiments confirm most aspects of the kinetics of our deuterium system, in particular the presence of an inverse chloride ion dependence on the rate of exchange. However, these authors [6] also report an approximate first-order acid dependence for the exchange, particularly at low acid concentrations, and claim that their observed kinetics indicates the absence of multiple exchange in benzene. However, a severe limitation of the tritium system is that multiple exchange cannot be directly observed since the concentration of tritium is such that the probability of more than one tritium being incorporated into a molecule is remote even if exchange were extensive. In our deuterium system such processes can be measured directly in the mass spectrometer. From their data, Gold and his co-workers [6] conclude that our formulations of the mechanisms of the catalysis in the deuterium exchange system are incorrectly deduced and that they are incompatible with the kinetic results.

Because of this apparent conflict, we present here further exchange data relevant to the issues raised by Gold and his co-workers.[6] A brief discussion of this problem was presented at the Sixth International Congress on Catalysis and subsequently published in the Proceedings.[11]

EXPERIMENTAL

Details of the procedures adopted for homogeneous exchange with platinum [2,4,9] rhodium,[12] and iridium [13] salts have been published. The quantities of reagents used in the various systems and exact conditions are specified in the relevant tables. Reagents were carefully checked for purity before use. Tetrachloroplatinate(II) salts were purified by recrystallisation from appropriate solutions. Reaction mixtures were sealed *in vacuo* in preconstricted glass ampoules and held in thermostatted ovens. The organic substrate recovered from the reaction mixture was analysed by low voltage mass spectrometry and proton n.m.r. as described elsewhere.[7] The multiple exchange parameter, M, was calculated by the methods described previously.[14]

RESULTS AND DISCUSSION

Evidence for Multiple Exchange.—The results for the exchange of a wide variety of aromatic compounds in the D_2O/CH_3CO_2D solvent system with tetrachloroplatinate(II) ion as catalyst are presented in Table 1. Cyclohexane is included for comparison purposes to show the reactivity of a cyclic saturated compound. The distribution of deuterium between species containing various numbers of deuterium atoms as indicated by the mass spectral data together with the M value calculated from the distribution for benzene show unequivocally the presence of multiple exchange. The orientation of isotope in monosubstituted aromatics is predominantly to *meta*- and *para*-positions as discussed previously.[1,3,4] In a consistent manner, M values significantly greater than unity have also been observed for the exchange of aliphatic compounds with tetrachloroplatinate(II) ion and for the exchange of aromatic compounds with homogeneous iridium and rhodium catalysts (Table 2).

TABLE 1

Exchange catalysed by K_2PtCl_4 in 24 mol % AcOD–D_2O and 4.6M-DCl at 130 °C for 16 h [a]

Compound	%D	Deuterium distribution						
		D_0	D_1	D_2	D_3	D_4	D_5	D_6
Benzene [b]	20.5	43.9	20.9	16.3	10.7	5.1	1.9	1.3
Toluene	18.1	23.1	34.6	24.7	11.8	4.2	1.2	0.4
m-Xylene	19.3	8.3	28.2	37.2	20.5	7.2		
Chlorobenzene	15.9	48.5	29.1	17.6	5.0			
t-Butylbenzene	13.1	55.0	29.5	11.5	3.3	0.6	0.1	
Anisole	51.9	3.4	14.6	28.8	30.6	17.7	4.9	
Pyridine	0.1	99.5	0.5					
Cyclohexane	0.8	91.8	7.1	1.0				

[a] $[K_2PtCl_4]$ = 0.02M, [organic] = 16% (w/w) in catalyst solution. [b] Multiple exchange parameter (M) = 1.7.

TABLE 2

Deuterium exchange with homogeneous rhodium and iridium catalysts

Catalyst	Compound	%D	Deuterium distribution									M
			D_0	D_1	D_2	D_3	D_4	D_5	D_6	D_7	D_8	
Rhodium [a]	Benzene	3.8	88.6	6.6	1.9	0.7	0.5	0.8	0.8			2.0
Rhodium [b]	Toluene	4.35	83.5	9.3	3.2	1.4	0.9	0.9	0.3	0.2	0.2	
Iridium [c]	Benzene	30.6	42.3	13.2	10.6	9.4	8.6	8.6	7.2			2.8
Iridium [d]	Toluene	11.5	59.7	13.1	11.4	9.6	3.9	2.8				

[a] $[RhCl_3{\cdot}3H_2O]$ = 0.02M in 50 mol % AcOD in D_2O: 0.2 ml of organic and 2 ml of catalyst solution at 131°C for 40 h. [b] As for *a* except 135 °C for 24 h. [c] $[Na_2IrCl_6]$ = 0.02M in 25 mol % AcOD in D_2O: 0.2 ml of organic and 2 ml of catalyst solution at 129 °C for 24 h. [d] As for *c* except 44 h.

In addition, we have found that the magnitude of the M value is independent of the volume of the vapour space in the reaction ampoule. In a series of experiments, the size of the liquid-vapour interface was varied by comparing ampoules held horizontally with those held vertically in the reaction oven. Ampoules were also shaken and in some reactions, exchanges were performed in ampoules designed to be ' vapour free '. A complete independence of the pattern of exchange with volume of vapour space was observed for aromatic and aliphatic systems and with homogeneous platinum, iridium, and rhodium catalysts. It thus appears indisputable that multiple exchange is a general property of certain *homogeneous* catalyst exchange systems, in the manner that it is of *heterogeneous* catalysed exchange and that it cannot be explained in terms of a non-equilibrated distribution of reactants between vapour and liquid phases as suggested by Gold and his co-workers.[6]

The presence of an inverse chloride-ion dependence in the kinetics of exchange in the tritium system [6] does not mitigate against multiple exchange, since the mechanism we propose satisfactorily explains this observation. The occurrence of a fast pre-equilibrium step involving loss of Cl^-, as discussed below, will suffice.

Stability of Platinum(II) *in Solution.*—The ease of precipitation of Pt^0 from homogeneous $PtCl_4^{2-}$ solutions under exchange conditions where water alone is the solvent has been noted.[2] Gold and his co-workers [6,7] state that only runs in which there was no precipitation of platinum during their reactions are reported and their discussion implies that visual examination was the only criteria for rejection. The possibility of *heterogeneous* exchange on colloidal platinum was not considered.

We have found it difficult in the absence of added acid to deuteriate benzene using $PtCl_4^{2-}$ with only D_2O as both the isotope source and solvent. In the absence of additional stabilisers, such as acetic acid, some platinum(0) is precipitated before 5—10% D is incorporated into benzene. This result is not surprising since $PtCl_4^{2-}$ is thermodynamically unstable in water [15] and will disproportionate to $PtCl_6^{2-}$ and Pt^0. Under the conditions studied by Ginstrup and Leden [15] equilibrium for equation (1) was established after *ca.* 1 month at 60 °C.

$$2PtCl_4^{2-} \rightleftharpoons PtCl_6^{2-} + Pt^0 + 2Cl^- \tag{1}$$

In 2M $[Cl^-]$, *ca.* 10% of the platinum is present as Pt^0 at equilibrium.

It has been reported [9] that in D_2O, $PtCl_6^{2-}$ will convert benzene into deuteriated chlorobenzene and deuteriated biphenyl. Likewise, a solution of $PtCl_4^{2-}$ in D_2O formed the same by-products as $PtCl_6^{2-}$, when no stabilising acids were present. With both $PtCl_6^{2-}$ and $PtCl_4^{2-}$ the by-products were formed in the same ratio and with the same deuterium distributions. This observation implied disproportionation to $PtCl_6^{2-}$ preceded any reduction directly to Pt^0 in the $PtCl_4^{2-}$ solutions.

Furthermore, the data presented in Figure 1 show clearly the activity of Pt^0 in catalysing exchange of benzene in aqueous media even in the presence of HCl. The Pt^0 used in this study was prepared by hydrogen activation of PtO_2 using the conditions previously described.[16] A more detailed comparison of the relative exchange rates of benzene with heavy water over a variety of Pt^0 catalysts [17] shows that less than 10^{-8} g of Pt^0 is all that is required to produce the exchange rates which would be attributed to $PtCl_4^{2-}$ in a non-stabilised homogeneous system such as that reported by Gold and his co-workers [6] and similar to the initial systems studied by ourselves. From our earlier experiments it was obvious to us that there are conditions possible in the $PtCl_4^{2-}$ system where platinum(0) is present at levels which are not readily visible, but in sufficient quantity to produce a small degree of *heterogeneous* catalysed exchange. Thus, where the observed approach to equilibrium in an exchange is very small (10^{-5}), as observed by Gold and his co-workers [6] in their tritium study, it is essential to be able to establish very carefully that the observed exchange is not due to traces of platinum(0) by establishing criteria to separate *homogeneous* from *heterogeneous* catalysed processes.

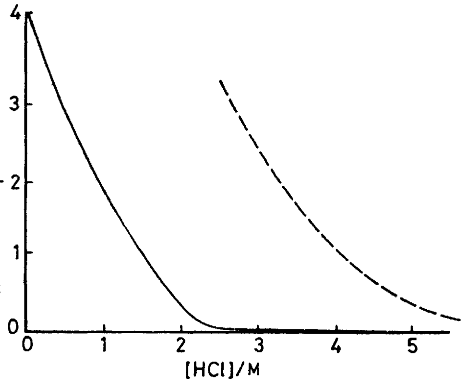


FIGURE 1 Inhibition of Pt^0-catalysed exchange of benzene by HCl in D_2O, full-line 32 °C, dashed-line 130 °C. [2 ml benzene, 10% by weight in HCl–D_2O, 20 mg Pt^0]

Evidence for the Absence of Exchange in the Presence of Precipitated Platinum(0) *in Acetic Acid Solutions*.—The ability to distinguish between *homogeneous* $PtCl_4^{2-}$ and *heterogeneous* Pt^0-catalysed exchange firstly involved the careful choice of a suitable solvent system which poisoned the catalytic activity of Pt^0. With this system, a detailed comparison of a number of the properties of both *homogeneous* and *heterogeneous* systems was performed. These included: (*a*) a consideration of the relative exchange rates of various aromatics such as chlorobenzene, benzene, nitrobenzene, anisole, and acetophenone, (*b*) a study of isotope orientation and relative exchange rates in the polycyclic aromatic hydrocarbons, particularly *o*-terphenyl and naphthalene and, (*c*) the significance of the multiple exchange parameter M. Much of the relevant data has been summarised previously [18] but additional results to support the above conclusions are shown in Tables **3** and **4**. Thus the M value for benzene is much higher in the homogeneous systems. Nitrobenzene, acetophenone, and bromobenzene all show little or no exchange with *heterogeneous* platinum at 130 °C whereas *homogeneously* all three compounds label extensively in the *meta*- and *para*-positions. Naphthalene exchange is retarded on *heterogeneous* platinum whilst *homogeneously* isotope incorporation is relatively rapid. Orientation effects can also be used to distinguish both catalytic systems; thus with *o*-terphenyl only in the *heterogeneous* systems are all protons of the centre ring capable of exchanging during the initial stages of the reaction.[19] All these observations have been rationalised in terms of the appropriate π-complex mechanism for each catalytic system.[18] The data show that we have been able to differentiate between

TABLE 3

Comparison of homogeneous and heterogeneous platinum catalysed exchange at 130 °C

		Homogeneous [a]		Heterogeneous [b]	
Series	Compound	Time (h)	%D	Time (h)	%D
A	Benzene	8	13.3	3.5	50.0
	Fluorobenzene	8	9.7	3.5	45.3
	Chlorobenzene	8	8.7	3.5	29.9
	Bromobenzene	8	9.8	3.5	1.4
B	Benzene	3	68.0	3.5	50.0
	Nitrobenzene	10	54.1	10	0.1
	Naphthalene	10	66.7	10	2.6
	Acetophenone	2	51.1		

[a] Homogeneous conditions series A: $[K_2PtCl_4] = 0.02M$, $[HCl] = 4.6M$, in 24 mol % AcOD–D_2O; 0.2 ml organic and 2 ml catalyst solution. Series B: $[Na_2PtCl_4] = 0.02M$, $[HCl] = 0.02M$, in 50 mol % AcOD–D_2O; 0.3 ml organic and 0.5 ml catalyst solution. [b] Heterogeneous conditions: Hydrogen-reduced PtO_2 (0.1 g), organic (1 g) in D_2O such that theoretical equilibrium %D = 50.

TABLE 4

Exchange catalysed by K_2PtCl_4 in 50 mol % AcOD–D_2O and 1.5M-DCl at 82 °C [a]

			Deuterium distribution						
Compound	Wt. (g)	%D	D_0	D_1	D_2	D_3	D_4	D_5	D_6
Benzene [b]	0.176	10.7	82.2	2.6	2.8	2.9	3.1	3.5	2.9
Fluorobenzene	0.205	5.9	87.6	3.1	3.6	4.0	1.5	0.2	
Chlorobenzene	0.221	5.7	87.1	3.0	3.7	6.0			
Bromobenzene	0.300	7.3	82.6	4.6	5.8	6.8		6.8	
Toluene	0.173	4.7	84.6	4.1	4.4	4.8	1.1	0.7	0.4
t-Butylbenzene	0.172	1.9	87.6	3.1	4.4	5.0			
Trifluorotoluene [c]	0.238	3.4	92.8	1.9	1.9	3.8			
Nitrobenzene [c]	0.200	7.3	84.8	2.6	4.2	8.1	0.2		

[a] Catalyst solution: 2 ml $[K_2PtCl_4] = 0.15M$ in 50 mol % AcOD in D_2O; Reaction time 4 h. [b] Multiple exchange parameter for benzene (M) 3.5. [c] Reaction temp. 80 °C.

$PtCl_4^{2-}$ and platinum(0) systems and thus clearly characterise *homogeneous* exchange in circumstances where *heterogeneous* exchange is suppressed. Moreover, it has been shown that the technique for distinguishing between *homogeneous* and *heterogeneous* platinum systems can also be extended to rhodium,[12] ruthenium,[20] and iridium,[20] and thus the concept is *generally* applicable to metal catalysis. For comparison purposes between *homogeneous* and *heterogeneous* systems, data are presented in Table 5 which illustrate the relative catalytic activities of Pt^0, Pt^{II}, and Pt^{IV} under equivalent conditions where CH_3CO_2D–D_2O is the solvent.

TABLE 5

Comparison of activity of platinum catalyst in benzene exchange under equivalent conditions [a]

Catalyst	Weight of catalyst (g)	% D in benzene
Pt^0	0.02	1.3
K_2PtCl_4	0.03	10.1
H_2PtCl_6	0.03	0.08
Nil		0.05

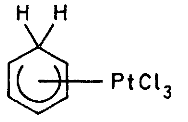
[a] Reaction conditions: 15 h at 110 °C, benzene (0.5 g) and 2 ml of 42 mol % AcOD–D_2O, 2.8M-DCl.

Table 4 also shows that exchange rate for nitrobenzene is similar to that of toluene and we conclude that the mechanism does not follow the traditional mechanisms for acid catalysed exchange.

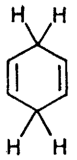
Significance of Reaction Temperature.—The exchange of organic compounds with $PtCl_4^{2-}$ in CH_3CO_2D–D_2O solvent proceeds steadily in the temperature region 60—120 °C, an M value of 3.5 being typical [2] of benzene at 82 °C (Table 4). A slightly higher M value [2] would be expected at 50 °C, the temperature used by Gold and his co-workers for their tritium experiments. By contrast, at 35 °C, a much lower M value of 1.5 for benzene exchange with D_2O on platinum metal is observed. Unfortunately, direct evidence for the degree of multiple exchange in the tritium system was not provided due to the low isotope concentrations. However, if M values close to unity did pertain, as the authors indicate,[6] then the result suggests platinum(0) rather than platinum(II) catalysis.

Types of Intermediates in Aromatic Exchange.—In the formulation of the mechanism of $PtCl_4^{2-}$-catalysed aromatic exchange involving plausible intermediates, a number of our earlier results are particularly relevant. Thus similar rates of exchange are observed for a number of compounds which contain markedly different activating and deactivating groups in their aromatic rings (Tables 1 and 4). Pronounced *ortho*-deactivation due to steric hindrance is found in most substituted aromatic compounds. Exchange readily propagates to the side chain of the alkyl aromatics.[7] A consideration of these observations leads us to reject, for our CH_3CO_2D–D_2O exchange system, the predominant participation of the following intermediates proposed by Gold and his co-workers for their tritiated water system.

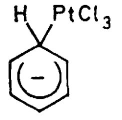
Species I which is formed by H^+ attack on $[(\pi\text{-}C_6H_6)\text{-}PtCl_2)]^-$ is the associative intermediate in our original homogeneous π-associative exchange mechanism.[2] However, as we have previously discussed in detail,[18] we preferred the predominant involvement of a dissociative-type intermediate since species (I) is not consistent with *ortho*-deactivation. In terms of the formation of species (I), a much larger attacking electrophile, but not H^+, might lead to deactivation of the *ortho*-position on steric grounds. Likewise, H^+ attack to form species (I) might be expected to show a considerable dependency on the electronic nature of the substituents on the ring, contrary to experimental observation.



(I)



(II)



(III)

With respect to species (II) which is formed by proton attack on (III), this is not compatible with *ortho*-deactivation in monosubstituted benzenes nor with the exchange patterns observed with *m*-xylene and biphenyls.[19,21] Furthermore, very detailed studies of electron capture by metal-containing organic compounds using secondary electron-capture negative-ion mass spectrometry [22] suggest that the charge would be localised preferentially on the halogen or platinum rather than on the ring as proposed [6] in species (III), thus rendering this latter intermediate less susceptible to proton attack on the ring. We therefore conclude that a study of the single compound, benzene, as carried out by Gold *et al.* is insufficient to clarify the intermediate species, and that our detailed study of a large variety of compounds shows that the participation of species (I)—(III) in the exchange mechanism is unlikely.

Furthermore, our mechanisms developed for *homogeneous* exchange closely resemble the corresponding mechanisms developed previously for analogous *heterogeneous* processes,[18] for which there is now a large amount of supporting experimental evidence. The diene intermediate, (II), proposed by Gold and his co-workers and their concept of activation of the π-complexed ring towards electrophilic substitution would be difficult to extend to the side-chain of the long-chain alkylbenzenes and also the simple alkanes. Their intermediates are not consistent with the *heterogeneous* analogues.

Interpretation of Kinetics in Terms of Exchange Mechanism.—We have proposed detailed mechanistic schemes to explain the first-order dependence in chloride ion for exchange in different types of organic compounds. The interpretation of the complex dependence on hydrogen ion [2] we believe to be complicated by the influence of hydrogen ion on the stability of $PtCl_4^{2-}$ towards disproportionation and precipitation as platinum(0). The most favoured scheme for benzene is depicted in Figure 2. The first step (A) in this process is the formation of an active species by interaction of the $PtCl_4^{2-}$ with the solvent. This species is represented as $PtCl_3S^-$ but the exact nature of this entity is the subject of considerable speculation,[9] and may be disolvated or dimeric in nature.

Justification for this mechanism has been discussed in detail elsewhere.[9] Clearly, since the concentration of the active species $PtCl_3S^-$ formed in a rapid pre-equilibrium step is inversely dependent on $[Cl^-]$, the overall rate of incorporation of deuterium by the rate-determining step (B) is first-order in tetrachloroplatinate-(II) and inverse first-order in chloride ion. The rate of step (C) relative to step (B) determines the degree of multiple exchange. This mechanism developed for benzene deuteriation has been readily adapted to explain exchange in a variety of other organic compounds including the monosubstituted benzenes, polycyclic aromatic hydrocarbons, alkylbenzenes both long- and short-chain, and the alkanes.[1-14,23,24]

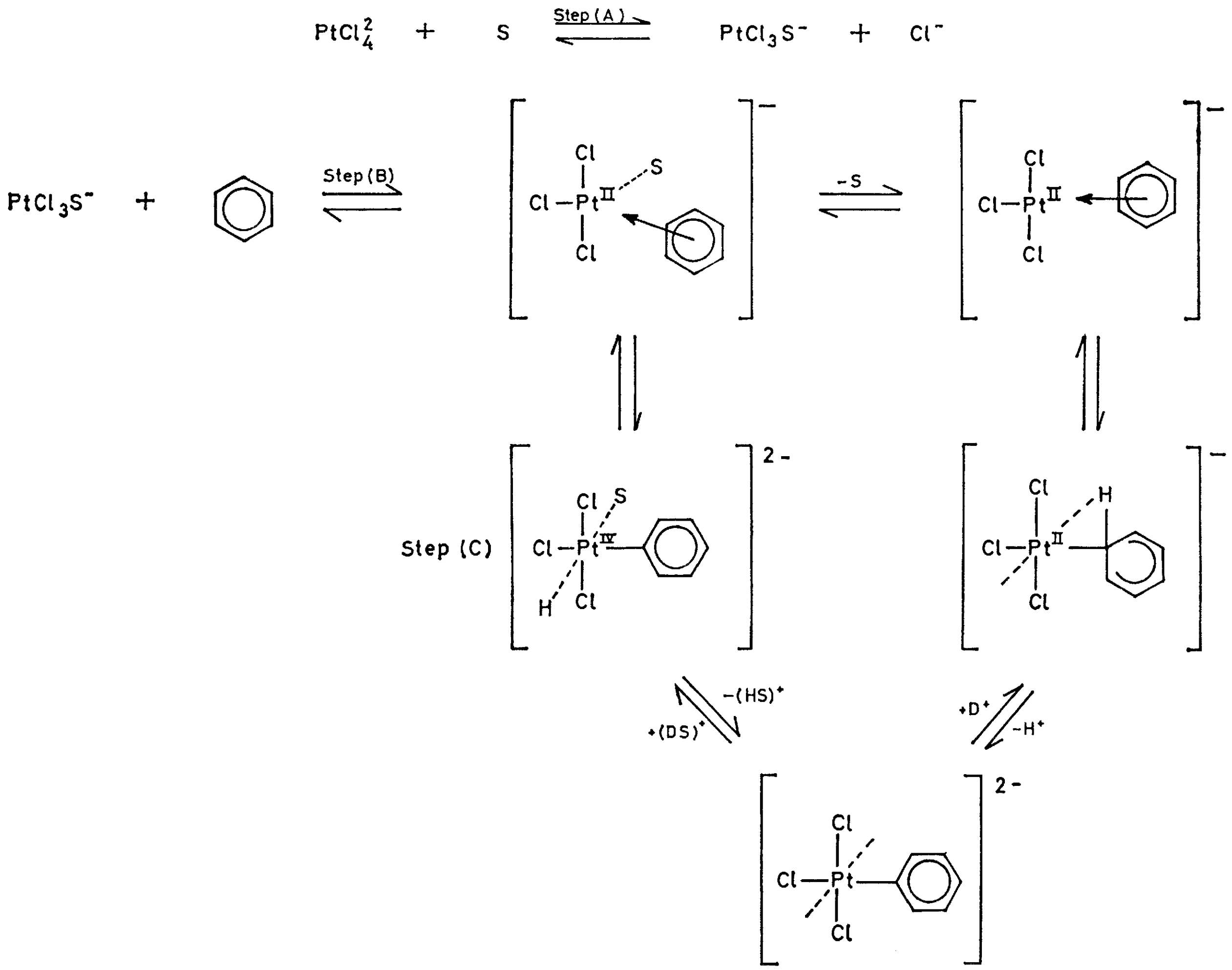


FIGURE 2 Mechanism for benzene exchange with homogenous Pt

The system described by Gold and his co-workers involving benzene exchange with tritium is different in a number of significant respects to the acetic acid–water reactions we have studied. The $[Cl^-]$ is some 50—100 fold greater in the tritiated water system and no acetic acid is present. It would thus appear that different ligands may be involved in their active catalytic species, leading to displacement of the complexed aromatic before multiple exchange can occur. The lifetime of the Pt–aromatic species, especially at high $[Cl^-]$, may then be comparable to the time required for the isotope substitution step. Some dependence of the observed exchange rate on $[H^+]$ might then be expected.

It is thus possible to interpret the kinetic data of Gold and his co-workers on the basis of the mechanisms we have proposed, including a rationalisation of the $[H^+]$ dependence. Gold and his co-workers [6] point out that the mechanism they have proposed does not permit an interpretation of multiple exchange, a phenomenon present in all reported $PtCl_4^{2-}$ deuterium exchange systems, both aromatic and aliphatic. The data, together with the fact that the rate of attainment of equilibrium in the tritium system is so very small, suggest that a significantly different catalytic process may be involved in the tritium system. We have reservations about this conclusion and we feel that they can only be clarified when it has been unequivocally established that the exchange reaction in the tritium system [6] does not involve a *heterogeneous* component.

We thank the Australian Research Grants Committee and the Australian Institute of Nuclear Sciences and Engineering for the support of this research.

[8/1032 *Received, 2nd June*, 1978]

REFERENCES

[1] J. L. Garnett and R. J. Hodges, *J. Amer. Chem. Soc.*, 1967, **89**, 4546.

[2] R. J. Hodges and J. L. Garnett, *J. Phys. Chem.*, 1968, **72**, 1673.

[3] R. J. Hodges and J. L. Garnett, *J. Catalysis*, 1969, **13**, 83.

[4] R. J. Hodges and J. L. Garnett, *J. Phys. Chem.*, 1969, **73**, 1525.

[5] P. A. Kramer and C. Masters, *J.C.S. Dalton*, 1975, 849.

[6] L. Blackett, V. Gold, and D. M. E. Reuben, *J.C.S. Perkin II*, 1974, 1869.

[7] J. L. Garnett and R. S. Kenyon, *Austral. J. Chem.*, 1974, **27**, 1023; 1033.

[8] R. J. Hodges, D. E. Webster, and P. B. Wells, *J. Chem. Soc.* (*A*), 1971, 3230.

[9] J. L. Garnett and J. C. West, *Austral. J. Chem.*, 1974, **27**, 129.

[10] R. J. Hodges, Ph.D. Thesis, University of New South Wales, Australia, 1969.

[11] J. L. Garnett, Proceedings Sixth International Congress Catalysis, London, 1976, p. 913.

[12] M. R. Blake, J. L. Garnett, I. K. Gregor, W. Hannan, K. Hoa, and M. A. Long, *J.C.S. Chem. Comm.*, 1975, 930.

[13] J. L. Garnett, M. A. Long, and K. B. Peterson, *Austral. J. Chem.*, 1974, **27**, 1823.

[14] M. A. Long, R. B. Moyes, P. B. Wells, and J. L. Garnett, *J. Catalysis*, 1978, **52**, 206.

[15] O. Ginstrup and I. Leden, *Acta Chem. Scand.*, 1967, **21**, 2689.

[16] J. L. Garnett and W. A. Sollich, *J. Catalysis*, 1963, **2**, 339.

[17] J. L. Garnett and W. A. Sollich, *Austral. J. Chem.*, 1961, **14**, 441; 1965, **18**, 993.

[18] J. L. Garnett, *Catalysis Rev.*, 1971, **5**, 229.

[19] K. P. Davis and J. L. Garnett, *J.C.S. Chem. Comm.*, 1975, 79.

[20] M. R. Blake, J. L. Garnett, M. A. Long, and K. B. Peterson, unpublished results.

[21] K. P. Davis and J. L. Garnett, *Austral. J. Chem.*, 1975, **28**, 1699; 1713.

[22] D. R. Dakternieks, I. W. Fraser, J. L. Garnett, and I. K. Gregor, *Talanta*, 1976, **23**, 701 and related papers in this series.

[23] C. A. Tolman, *Chem. Soc. Rev.*, 1972, **1**, 337.

[24] G. W. Littlecott and F. J. McQuillin, *Tetrahedron Letters*, 1973, **50**, 5013.