Kinetics of Hydrogen Isotope Exchange Reactions. Part XXVI.[1] Catalysis of Tritium Exchange between Benzene and Solvent Water by Potassium Tetrachloroplatinate(II)

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Tritium uptake by benzene, dissolved in acidified tritiated water containing chloride ions at 50°, is catalysed by tetrachloroplatinate(II) ions. The first-order exchange rate constant λ is approximately proportional to the concentrations of catalyst and hydrogen ion and inversely proportional to the concentration of chloride ions. The reaction mechanism required by these reaction orders involves at least one (and probably two) low-concentration intermediates of the composition $(C_6H_6{-}PtCl_3)^-$ and (at low acid concentrations) the rate-limiting protonation of such an intermediate. Possible structures of the various reaction intermediates are indicated.

CATALYSIS of aromatic hydrogen exchange between benzenoid compounds and solvent by dissolved Pt^{II} salt has been reported by Garnett and Hodges [2] and fully reviewed by Garnett.[3] The reactions were followed by measuring the uptake of deuterium by the aromatic compound from deuterium oxide in the solvent (which also contained acetic acid) by mass spectrometric analysis. The instability of tetrachloroplatinate(II) and the comparative slowness of the exchange reaction led the authors to employ media of high acid concentration, elevated temperatures, and high substrate concentrations. Hodges and Garnett [2d] concluded that the rate of deuterium uptake increased with the concentrations of benzene and tetrachloroplatinate(II) and was inversely proportional to that of chloride ion. The dependence of the rate on acidity was reported to be more complex, but it was concluded that the exchange itself is not acid-catalysed.[2a,3] Factors mentioned as being responsible for the acidity effect were the precipitation of platinum at low acidities, dielectric constant, solubility, and competition by the normal acid-catalysed [4] route.

For a kinetic study of the Pt^{II} catalysis we decided to attempt experiments in a simpler solvent system (*viz.* water), and at a lower temperature (50°). The required conditions could be achieved by use of tracer tritium, the ease of assay of which makes it possible to study initial rates of very slow reactions.[5,6] Potassium tetrachloroplatinate(II) solutions were found not to precipitate platinum, even when the solutions were only feebly acidic, provided chloride ions were added in fairly high concentration. These observations cause us to qualify Hodges and Garnett's statement that addition of 4M-hydrochloric acid is necessary to stabilise $PtCl_4^{2-}$ in aqueous solution, although it may nevertheless apply at the higher temperatures used in their work.

To anticipate our main conclusions, we fully confirm Garnett and Hodges' discovery of catalysis of aromatic exchange also in aqueous solution. However, we believe that their formulations of the mechanisms of this catalysis are incorrectly deduced and that they are incompatible with kinetic results. A general mechanistic scheme of the required kinetic form is now proposed.

EXPERIMENTAL

Potassium tetrachloroplatinate(II) (Johnson-Matthey) was dissolved in hot concentrated hydrochloric acid (AnalaR) and insoluble potassium hexachloroplatinate(IV), present as an impurity in the commercial platinum(II), was filtered off. Potassium tetrachloroplatinate(II) was crystallised from the acid and vacuum-dried. Benzene was shaken out with five successive lots of concentrated sulphuric acid and then several times with water before being dried (molecular sieve 4 A) and then subjected to g.l.c. (F and M 770; Carbowax). Tritiated water was obtained from the Radiochemical Centre, Amersham. Water was triply distilled; other reagents were of AnalaR quality.

Kinetic experiments were performed in vapour space-free ampoules (30 cm^3), tightly closed with Rotaflo Teflon stopcocks.[7] Solutions were made up by weight and transferred by syringe. The isolation of benzene from the reaction mixture after a fixed time and subsequent tritium assay essentially followed previously established procedures.[7] Results are reported only for experiments in which there was no precipitation of platinum during the reaction.

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[1] Part XXV, V. Gold and M. A. Major, *J.C.S. Faraday I*, 1974, **70**, 977.

[2] J. L. Garnett and R. J. Hodges (*a*) *J. Amer. Chem. Soc.*, 1967, **89**, 4546; (*b*) *Chem. Comm.*, 1967, 1001; (*c*) *ibid.*, p. 1220; R. J. Hodges and J. L. Garnett (*d*) *J. Phys. Chem.*, 1968, **72**, 1673; (*e*) *ibid.*, 1969, **73**, 1525; (*f*) *J. Catalysis*, 1969, **13**, 83.

[3] J. L. Garnett, *Catalysis Rev.*, 1971, **5**(2), 199.

[4] For a review see V. Gold in 'Friedel–Crafts and Related Reactions,' ed. G. A. Olah, Interscience, New York and London, 1964, vol. 2, p. 253.

[5] V. Gold and L. C. Gruen, *J. Chem. Soc.* (*B*), 1966, 600.

[6] J. R. Adsetts and V. Gold, *J. Chem. Soc.* (*B*), 1969, 950.

[7] C. L. Brett and V. Gold, *J.C.S. Perkin II*, 1973, 1437.

RESULTS

The first-order exchange rate constants λ were evaluated[5] from initial rates according to equation (1), where f is the fractional progress of the reaction towards equilibrium.

$$\lambda = \mathrm{d}f/\mathrm{d}t = (f/t)_{t \to 0} \qquad (1)$$

If A expresses the activity (disintegrations min^{-1}, d.p.m.) per g equiv. of benzene (1/6 mol) and A_w the corresponding activity of water (initial or final since solutions are dilute), f is given by equation (2). This involves the operationally convenient approximation that completion of

$$f = A/A_w \qquad (2)$$

exchange ($f = 1$) corresponds to equality of tritium abundance amongst all exchanging positions, *i.e.* that the equilibrium isotope effect may be neglected. Since 1 Ci $\equiv 2{\cdot}22 \times 10^{12}$ d.p.m., a solution containing w Ci dm^{-3} at 25° has a value of A_w of $2{\cdot}22 \times 10^{12}w \times 9/997$ d.p.m. (g equiv.)$^{-1}$, whence $f = 49{\cdot}9 \times 10^{-12}A/w$ and $\lambda = (49{\cdot}9 \times 10^{-12}/w).\mathrm{d}A/\mathrm{d}t$. Counting efficiencies for benzene were *ca.* 50%.

The expected linear dependence of f upon t [equation (1)] for small values of f is exemplified in Figure 1. Groups of runs performed on the same batches of material under identical conditions generally showed good internal consistency. In our view less importance is to be attached to the variation between results belonging to different groups of runs (*cf.* the various experiments at the same concentration in different Tables). For runs at acid concentrations higher than those listed, the competing acid catalysed exchange is not negligible, but even in 7M-hydrochloric acid there is catalysis by potassium tetrachloroplatinate(II), observable as an additional rate enhancement (Figure 2). Acid catalysis is negligible in 1M-acid, the concentration used for most of the experiments reported in this paper.

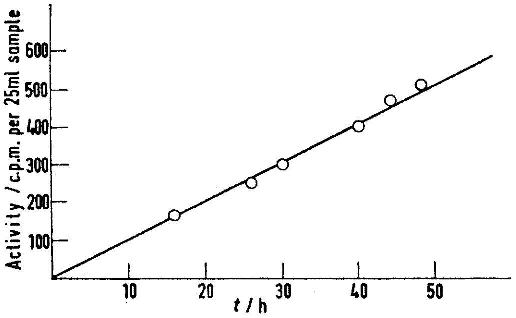


FIGURE 1 Sample activity as function of time for exchange in low-acidity medium ([HCl] = 0·01M; [LiCl] = 2M; [K_2PtCl_4] = 0·02M; w = 4 Ci dm^{-3})

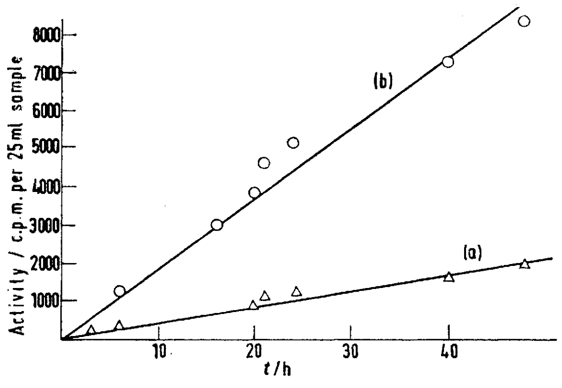


FIGURE 2 Exchange in 7M-HCl: (a) without addition; (b) in the presence of 0·02M-K_2PtCl_4

Radiation-induced hydrogen exchange is absent at the comparatively low tracer levels employed, as shown by the fact that the rate constant λ is independent of the concentration of tritium label in the water. Tables 2—4 illustrate that λ is independent of the concentration of benzene, that it is nearly proportional to the concentration of potassium tetrachloroplatinate(II), and to the reciprocal of the concentration of chloride ion, as indicated in each case by the near constancy of the values in the final column. In these groups of experiments one concentration was being varied at a time, all others being kept constant. Table 5 gives some of the results for the dependence of λ upon the concentration of hydrogen ion. Except where specified otherwise

TABLE 1

Dependence of λ on tritium concentration

w / Ci dm^{-3}	$\mathrm{d}A/\mathrm{d}t$ / d.p.m. (g equiv.)$^{-1}$ s^{-1}	$10^9\lambda$ / s^{-1}
0·98	60	3·1
1·97	139	3·5
3·94	242	3·1
7·82	440	2·8

TABLE 2

Dependence of λ on benzene concentration

[HCl] = 1·02M

$10^3[C_6H_6]$ / M	$\mathrm{d}A/\mathrm{d}t$ / d.p.m. (g equiv.)$^{-1}$ s^{-1}	$10^9\lambda$ / s^{-1}
1·9	135	1·7
3·85	153	1·9
5·8	159	2·0
7·7	146	1·8

TABLE 3

Dependence of λ on Pt^{II} concentration

$10^3[K_2PtCl_4]$ / M	$\mathrm{d}A/\mathrm{d}t$ / d.p.m. (g equiv.)$^{-1}$ s^{-1}	$10^9\lambda$ / s^{-1}	$10^6\lambda/[Pt^{II}]$ / s^{-1} mol^{-1} dm^3
5	82	1·0	0·21
10	164	2·1	0·21
20	241	3·1	0·15
40	392	5·0	0·12

TABLE 4

Dependence of λ on chloride concentration

([HCl] + [$HClO_4$]) = 1·0M; w = 3·86 Ci dm^{-3}

[HCl] / M	$\mathrm{d}A/\mathrm{d}t$ / d.p.m. (g equiv.)$^{-1}$ s^{-1}	$10^9\lambda$ / s^{-1}	$10^9\lambda[Cl^-]$ / s^{-1} mol dm^{-3}
0·02	13,515	174·6	3·5
0·04	5,269	68·1	2·7
0·10	1·679	21·7	2·2
0·20	858	11·1	2·2
0·40	518	6·7	2·7
0·60	339	4·4	2·6
0·70	343	4·4	3·1
0·80	283	3·7	2·9
0·90	235	3·0	2·7
1·00	209	2·7	2·7

TABLE 5

Dependence of λ on hydrogen ion concentration

([HCl] + [LiCl]) = 1·0M

[HCl] / M	$\mathrm{d}A/\mathrm{d}t$ / d.p.m. (g equiv.)$^{-1}$ s^{-1}	$10^9\lambda$ / s^{-1}	$10^9\lambda/[H^+]$ / s^{-1} mol^{-1} dm^3
0·1	24	0·31	3·1
0·2	42	0·53	2·6
0·5	91	1·15	2·3
1·0	140	1·77	1·8

in the Tables, all measurements refer to a temperature of 50° and to the following concentrations: [HCl] = 1M; $[K_2PtCl_4] = 0{\cdot}02M$; $[C_6H_6] = 7{\cdot}7 \times 10^{-3}M$; $w = 3{\cdot}94$ Ci dm^{-3}. The addition of potassium hexachloroplatinate(IV) was found not to have a significant effect upon the exchange rate (*cf.* following paper).

DISCUSSION

The observations detailed in the Tables confirm the reports by Garnett and Hodges [2] that tetrachloroplatinate(II) salts can catalyse aromatic hydrogen exchange between benzene and water in homogeneous solution. Our measurements relate to a different solvent system and to a lower temperature (50°) than the earlier work and, for this reason, detailed comparison with that work is not possible. In agreement with Hodges and Garnett [2d] we conclude that the rate of exchange is proportional to the concentration of benzene (Table 2) and increases almost in proportion to the stoicheiometric concentration of tetrachloroplatinate(II) salt (Table 3), and that it is inversely proportional to the concentration of chloride ion (Table 4). The use of water as solvent in our work enabled us to measure an uncomplicated acidity dependence of the exchange. The rate increases with the concentration of hydrogen ion, the variation being somewhat less than proportional (Table 5). This may point to the existence of a limiting acidity-independent exchange rate at high acid concentrations, which is also suggested by some of Hodges and Garnett's [2d] data and by some exploratory measurements of ours.

The mechanism of the exchange has previously been discussed by Garnett and Hodges who consider pathways on the basis of plausible structures for intermediates, but do not attempt to relate these pathways to observed reaction orders. They also attach great importance to their observation that the amounts of multiply-deuteriated benzenes formed during the early stages of the exchange of benzene with a fully deuteriated medium are larger than one would expect if the exchange reaction were a step-wise process in which one labelled atom is introduced into a benzene molecule during each rate-limiting step. Since our own experiments involved tritium exchange at the tracer level, they do not provide independent information on this interesting point for reactions in aqueous solution. Indirect evidence, now to be detailed, seems to suggest that such multiple labelling cannot be extensive in our system. As was correctly pointed out by Hodges and Garnett, the occurrence of multiple labelling *prima facie* implies that the initial complexing reaction is followed by several exchange cycles. Two sets of conditions seem to satisfy this postulate. *Either* the complexing step is rate limiting, and all subsequent steps rapid (which is incompatible with the observed reaction orders in our system), *or* the initially-formed complex is a stable species into which the larger part of the benzene in solution is converted, and this firmly 'adsorbed' benzene then undergoes exchange reactions. This situation is similar to the one considered in the classical Michaelis–Menten treatment of strong catalyst (E)–substrate (S) binding. It requires the rate of product formation at high concentration of either substrate or catalyst to reach a limiting (' saturation ') value, corresponding to the rate of decomposition of the complex. It may be significant that at high concentrations of Pt^{II}, with $[Pt^{II}] > [C_6H_6]$, our experiments appear to indicate a falling off in the order of the reaction with respect to Pt^{II} (see Table 3), but a limiting rate is not reached under our conditions.

Whilst these arguments may not apply in the different solvent system [and different relative concentrations of benzene and tetrachloroplatinate(II)] we are not certain that the observation of multiple labelling in Garnett and Hodges' experiments requires the mechanistic conclusion drawn by them. Our doubts stem from the fact that these reactions were carried out at temperatures near or above the b.p. of benzene, in sealed tubes of unspecified volume. If, as seems conceivable as a tentative conjecture, part of the substrate was confined to the vapour space (where exchange does not occur) and if phase equilibrium between dissolved benzene and benzene vapour is relatively slow, the probability of multiple exchange events in the system as a whole would not be representative of the reaction in solution. The curiously different patterns of multiple labelling in different hydrocarbon substrates (especially in non-volatile polycyclic hydrocarbons where step-wise exchange is reported [2f] to predominate over multiple exchange) might then receive a simple explanation. In our experience loss of volatile aromatic hydrocarbons into the vapour space of a sealed container can be serious and must be minimised [6] even at 25°; it was avoided in the present work by use of vapour-free ampoules.

We shall attempt to deduce the essential features of the exchange mechanism from the kinetic observations without preconceptions about their structural implications. According to the observed reaction orders we formulate the stoicheiometry of the transition state at low concentrations of acid as $\{C_6H_6, PtCl_3^-, H^+, \pm nH_2O\}$ and consider that at high acid concentrations the composition may become $\{C_6H_6, PtCl_3^-, \pm nH_2O\}$, corresponding to an acidity-independent process, or possibly $\{C_6H_6, PtCl_4^{2-}, \pm nH_2O\}$. The most straightforward explanation of these reaction orders is that the rate-limiting step in media of low acidity is a protonation reaction, whereas in media of high acidity this protonation is rapid and it is an earlier step in the reaction sequence which becomes rate-limiting.

Which of the two transition state compositions is correct for the acidity-independent process depends on whether the chloride inhibition observed with 1M-acid continues at high acidities. The observation that the Pt^{II}-catalysed exchange reaction in 7M-hydrochloric acid (Figure 2) is 2—3 times slower than the corresponding reaction in 1M-hydrochloric acid suggests that the chloride inhibition continues beyond the cessation of hydrogen-ion catalysis. This would be compatible with the transition-state composition $\{C_6H_6, PtCl_3^-, \pm nH_2O\}$ rather than with the alternative $\{C_6H_6, PtCl_4^{2-}, \pm nH_2O\}$. It must, however, be recognised that the total neglect of general electrolyte effects in such concentrated solutions may vitiate this conclusion, and it does not seem possible to resolve this ambiguity at present.

It is characteristic of potential-energy profiles of hydrogen isotope exchange reactions that they are symmetrical about a mid-point which corresponds to a configuration in which the incoming (isotopically labelled) and outgoing hydrogen atoms occupy equivalent positions.[4] The initial rate constant of such an exchange process (when reversal is negligible), defined by equation (1), is then given by the specific initial rate $k = v_+/[\mathrm{XH}]$ for the formation of the 'symmetrical' intermediate from the substrate XH, modified by a numerical factor β to express a kinetic isotope effect in the formation of the 'symmetrical' intermediate and in its decomposition in a forward or backward direction, according to equation (3).

$$\lambda = k\beta \tag{3}$$

The conclusions concerning the composition of transition states and the general form of exchange mechanisms are most simply accommodated by the formal Scheme 1 (applicable if the chloride inhibition persists at high acidities) or the slightly simpler Scheme 2 (which requires chloride inhibition to cease at high acidities). The equations for the individual reactions (4)—(7), which may themselves be composite, employ the following symbols: B stands for benzene, and $(\mathrm{B,PtCl_3})^-$

$$\mathrm{B} + \mathrm{PtCl_4}^{2-} \underset{-1}{\overset{1}{\rightleftharpoons}} (\mathrm{B,PtCl_3})^- + \mathrm{Cl}^- \tag{4}$$

$$(\mathrm{B,PtCl_3})^- \underset{-2}{\overset{2}{\rightleftharpoons}} (\mathrm{B,PtCl_3'})^- \tag{5}$$

$$(\mathrm{B,PtCl_3'})^- + \mathrm{H}^+ \underset{-3}{\overset{3}{\rightleftharpoons}} \mathrm{HB,PtCl_3'} \tag{6}$$

Scheme 1

$$\mathrm{B} + \mathrm{PtCl_4}^{2-} \underset{-1}{\overset{1}{\rightleftharpoons}} (\mathrm{B,PtCl_3})^- + \mathrm{Cl}^- \tag{4}$$

$$(\mathrm{B,PtCl_3})^- + \mathrm{H}^+ \underset{-4}{\overset{4}{\rightleftharpoons}} \mathrm{HB,PtCl_3} \tag{7}$$

Scheme 2

and $(\mathrm{B,PtCl_3'})^-$ are two isomeric complexes formed as low-concentration intermediates. The low-concentration complexes $\mathrm{HB,PtCl_3}$ and $\mathrm{HB,PtCl_3'}$ of equations (7) and (6) represent the mid-points of the respective potential-energy profiles, and the specific initial rates (k) of their formation are the parameters required for equation (3). As always in a formal analysis of this kind, the various unstable intermediates may additionally incorporate one or more water molecules.

Application of the stationary-state treatment to the three low-concentration intermediates of equations (4)—(6) leads to expression (8) for k, where the numbered rate coefficients correspond to the numbered steps in equations (4)—(7). At low values of the concentration of hydrogen ion, equation (8) may be simplified to (9),

$$k = \frac{k_1k_2k_3[\mathrm{PtCl_4}^{2-}][\mathrm{H}^+]}{k_{-1}[\mathrm{Cl}^-](k_{-2} + k_3[\mathrm{H}^+])} \tag{8}$$

$$k_{\mathrm{low}} = K_1K_2k_3[\mathrm{PtCl_4}^{2-}][\mathrm{H}^+]/[\mathrm{Cl}^-] \tag{9}$$

which implies that the protonation step 3 [equation (6)] is rate limiting. (K_1 and K_2 are equilibrium constants.) For high concentrations of hydrogen ion we obtain equation (10), corresponding to a rate-limiting re-

$$k_{\mathrm{high}} = K_1k_2[\mathrm{PtCl_4}^{2-}]/[\mathrm{Cl}^-] \tag{10}$$

arrangement 2 [equation (5)]. If the rearrangement step is absent, Scheme 2, consisting of reactions 1, —1, and 4 only, gives limiting equations (11) and (12), the former

$$k_{\mathrm{low}} = K_1k_4[\mathrm{PtCl_4}^{2-}][\mathrm{H}^+]/[\mathrm{Cl}^-] \tag{11}$$

$$k_{\mathrm{high}} = k_1[\mathrm{PtCl_4}^{2-}] \tag{12}$$

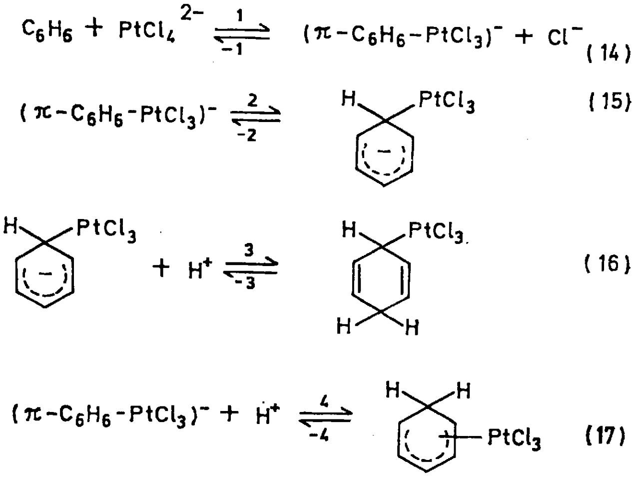
of which has the same concentration terms as equation (9), whereas equations (10) and (12) differ in the dependence on chloride-ion concentration.

The assignment of structural formulae to the intermediates must be more conjectural, but to demonstrate that the general scheme is acceptable, we must attempt to make such an assignment. The inverse dependence of the rate on chloride concentration might be thought to be connected with the well-studied ligand displacement[8] equilibrium (13), but the observation that the aquated

$$\mathrm{PtCl_4}^{2-} + \mathrm{H_2O} \rightleftharpoons \mathrm{PtCl_3(H_2O)}^- + \mathrm{Cl}^- \tag{13}$$

species is less reactive towards olefins than the tetrachloro-ion[9] makes its involvement in the reaction with benzene unlikely.

Equations (14)—(16) represent one specific version of Scheme 1 and (14), (18), and (19) another, with the numbered reaction steps referring to those of the general mechanism in equations (4)—(6). The equilibrium of equation (14) is assumed to be rapidly established.



The corresponding Scheme 2 would combine equation

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[8] L. I. Elding and I. Leden, *Acta Chem. Scand.*, 1966, **20**, 706; L. I. Elding, *ibid.*, 1970, **24**, 1331.

[9] D. Banerjee, F. Basolo, and R. G. Pearson, *J. Amer. Chem. Soc.*, 1957, **79**, 4055; R. M. Milburn and L. M. Venanzi, *Inorg. Chim. Acta*, 1968, **2**, 97.

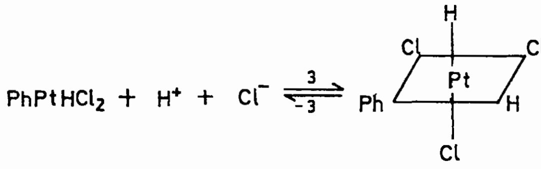
(14) with equation (17). The reaction product in equation (17) may perhaps best be regarded as a π-allylic or π-pentadienylic complex. In both these schemes it is implicit that the co-ordination to Pt^{II} activates the organic ligand towards electrophilic attack, probably through the increase in negative charge resulting from π-back-donation from platinum(II). Presumably this dominant increase in electron density in the organic portion overshadows polar effects of substituent groups on the benzene ring and renders the reaction insensitive to such polar effects.[2a,b,3]

The hypothesis of the importance of back-donation also emerges from the known electronic effect of structural modifications in the olefin on the stability of Pt^{II}–olefin complexes.[10] Electron-withdrawing substituents stabilise these complexes, which suggests that back-donation is more important than the formation of the olefin–platinum σ-bond. Equations (14) and (17) have also been put forward by Garnett and Hodges as a possible mechanism, although it is not clear how they could reconcile it with their own conclusion that the exchange is not acid-catalysed *and* its rate inversely proportional to chloride concentration.

A different chemical version of Scheme 2 is represented in equations (18) and (19), occurring subsequently to (14).

The Scheme involves 4- and 6-co-ordinate phenyl-(hydride) complexes of which, it must be admitted, no close analogues are known. It is, however, of the required kinetic form. Further, reactions 3 and —3 of equation (19) invoke the same kind of exchange pathway as Falk and Halpern [11] did to account for the hydrogen exchange [12] in *trans*-$(PEt_3)_2PtHCl$, which is catalysed by hydrogen and chloride ions.[11] (There are two equivalent pairs of H,Cl ligands in *trans*-positions, either of which can be eliminated in step —3.)

$$(\pi\text{-}C_6H_6\text{-}PtCl_3)^- \underset{-2}{\overset{2}{\rightleftharpoons}} PhPtHCl_2 + Cl^- \qquad (18)$$


(19)

We mention this mechanism because Garnett and Hodges based their mechanisms for aromatic hydrogen exchange on a supposed analogy with the Falk–Halpern scheme. However, the essential feature of that scheme, of two equivalent H,Cl ligands in the intermediate, is *not* retained in the different mechanism *via* a platinum(IV) complex containing phenyl and hydride ligands proposed by Garnett and Hodges. Furthermore, their mechanism is not in accord with the observed reaction orders.

It is probable that other mechanisms, equally compatible with the general Schemes of equations (4)—(7) could be devised.

[4/1265 *Received*, 26*th June*, 1974]

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[10] F. R. Hartley, 'The Chemistry of Platinum and Palladium,' Applied Science, London, 1973, pp. 375—376; R. G. Denning, F. R. Hartley, and L. M. Venanzi, *J. Chem. Soc.* (*A*), 1967, 324.

[11] C. D. Falk and J. Halpern, *J. Amer. Chem. Soc.*, 1965, **87**, 3003, 3523.

[12] J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 1959, 4020.