Kinetics of Hydrogen Isotope Exchange Reactions. Part XXVII.[1] Catalysis of Aromatic Tritium Exchange between Benzyl Alcohol and Solvent Water by Potassium Tetrachloroplatinate(II)

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Tritium uptake into the aromatic positions of benzyl alcohol from tritiated solvent water (containing some acid and chloride ions, at 50°) is catalysed by tetrachloroplatinate(II). The reaction shows a somewhat erratic induction period [due to platinum(IV) impurity] which is greatly increased by addition of potassium hexachloroplatinate(IV). Almost no exchange occurs during the induction period, so that for several days the reaction appears to be totally suppressed by Pt^{IV}. The results are interpreted in terms of the rate-limiting formation of a common intermediate (an adduct between benzyl alcohol and $PtCl_3^-$) which is oxidised by Pt^{IV} more rapidly than it can proceed to exchange hydrogen with the solvent. The rate of the exchange reaction (after the induction period) is approximately proportional to the concentration of $PtCl_4^{2-}$ and inversely proportional to the concentration of chloride ion. The dependence of the exchange rate on hydrogen-ion concentration is consistent with a protolytic equilibrium involving the alcohol group in a benzyl alcohol–$PtCl_3^-$ complex (p$K \geqslant 3{\cdot}6$), with the basic form being more reactive than its conjugate acid.

FOLLOWING our kinetic study [1] of Pt^{II}-catalysed tritium exchange between the aromatic hydrogen atoms of benzene and solvent water, it was intended to make a comparative investigation with a more water-soluble and less volatile aromatic substrate, in order to investigate the mechanism in greater detail. Our choice of substrate fell on benzyl alcohol and, as anticipated, it underwent aromatic exchange and proved a convenient solute for our procedure. However, it immediately became apparent that there were marked differences between the exchange kinetics of benzyl alcohol and those of benzene. The elucidation of the reaction mechanism proved to be a

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[1] Part XXVI, L. Blackett, V. Gold, and D. M. E. Reuben, preceding paper.

distinct problem rather than an extension of the earlier work. The preliminary results which led to this conclusion were as follows. The increase of the aromatic tritium content of benzyl alcohol with time was non-linear at quite low values of *f* (the fractional progress of the reaction towards equilibrium). The rate at first increased after the fashion of autocatalytic reactions and then became constant. The length of the initial induction period appeared to be somewhat erratic and, in particular, to vary between different batches of materials [potassium tetrachloroplatinate(II) and tritiated water]. It was not eliminated if all components of the reaction mixture with the exception of benzyl alcohol were mixed beforehand and the mixture placed in the thermostat for a time interval longer than the induction period and the reaction was subsequently started by addition of benzyl alcohol. On the other hand, an analogous pre-mixing, in which tritiated water was the only component initially left out, appeared largely to eliminate the induction period. Another preliminary observation indicated total inhibition of the exchange by addition of potassium hexachloroplatinate(IV) in very low concentration (*ca.* 1/20 of the concentration of the Pt^{II} salt), whereas addition of the possible oxidation product benzaldehyde was without effect on the exchange rate. The problems raised by these findings and their more complete investigation are further considered below.

EXPERIMENTAL

In most kinetic experiments benzyl alcohol (B.D.H.) was used without prior treatment since no significant differences in kinetic behaviour or analytical g.l.c. were found between the commercial sample and a specimen purified [2] by repeated extractions successively with 5% potassium hydroxide, saturated sodium chloride solution, sodium pyrosulphite and 5% sodium carbonate (both under nitrogen), and saturated sodium chloride solution, followed by drying ($MgSO_4$) and distillation under reduced pressure (5—10 mmHg).

The normal routine for kinetic measurements was to weigh solid solutes into a volumetric flask, add measured volumes of stock hydrochloric acid solution, benzyl alcohol, and water to bring the total volume to 100 cm^3, and the flask was securely closed and shaken (30 min). Tritiated water was added after this period and the flask was then shaken by hand before aliquot portions (20 cm^3 or, sometimes, 15 cm^3) were transferred (all-glass syringe with Teflon needle) to reaction vessels which were stoppered and placed in the thermostat bath at 50°. At the end of the reaction period the contents of the vessel were poured and rinsed (with saturated sodium chloride solution) into a test tube (100 cm^3), to which carrier benzyl alcohol (3 cm^3) was then added. The stoppered tube was shaken (30 min) to allow undissolved benzyl alcohol to equilibrate with the dissolved benzyl alcohol. The layers were separated, and the alcohol layer was extracted with ten successive portions (10 cm^3) of saturated sodium chloride solution in order to remove hydroxylic tritium. The separated benzyl alcohol was then dried (molecular sieve 4 A) for 3—4 days and portions (0·15 cm^3) were assayed for tritium.[3] An independent check of the extraction procedure, with inactive benzyl alcohol and tritiated water, established that this treatment completely removed hydroxylic tritium.

TABLE 3

Dependence of rate on substrate concentration

w 3·6 Ci dm^{-3}

[PhCH$_2$OH] / M	[Pt^{II}] / M	10^4[HCl] / M	[NaCl] / M	dA/dt / d.p.m. mol^{-1} s^{-1}	t_0 / h	10$^9\lambda$ / s^{-1}	10$^9\lambda$[Cl$^-$]/[Pt^{II}] / s^{-1}
0·0482	0·020	92	1·90	692	1	9·6	911
0·0963	0·020	92	1·90	697	1	9·7	918
0·0482	0·040	1	1·90	2080	12	28·8	1369
0·0963	0·040	1	1·90	3270	10	45·3	2153
0·0482	0·040	0·01	1·90	2560	14	35·5	1686
0·0963	0·040	0·01	1·90	4460	13	61·8	2936

Other procedures and materials were as in previous work.[1]

RESULTS

The results were again expressed in terms of the fractional progress of the reaction [as defined in equations (1) and (2) of the preceding paper]. Benzyl alcohol has several non-equivalent aromatic positions but for the purpose of defining *A* and *f* it was assumed that exchange in a single position is being observed (or is more rapid than exchange at other positions), *i.e.* the equivalent weight of benzyl alcohol was equated with its molecular weight. The assumption is arbitrary, since the position of the aromatic exchange was

TABLE 1

Comparison of activities of benzyl alcohol and benzoic acid (obtained from benzyl alcohol by permanganate oxidation)

Expt. no.	10$^{-5}A_{PhCH_2OH}$ / d.p.m. mol^{-1}	10$^{-5}A_{PhCO_2H}$ / d.p.m. mol^{-1}	Activity in ring / %
15	94	90	96
16	191	189	99
18	238	250	105
18	408	408	100

* See Table 4 for experimental conditions.

TABLE 2

Dependence of rate on tritium concentration w

[NaCl] = 1·90M

w / Ci dm^{-3}	[PhCH$_2$OH] / M	[Pt^{II}] / M	10^4[HCl] / M	dA/dt / d.p.m. mol^{-1} s^{-1}	t_0 / h	10$^9\lambda$ / s^{-1}
2·0	0·0963	0·04	9·2	1560	10	38·9
3·6	0·0963	0·04	9·2	2800	9	38·9
2·0	0·0482	0·02	92	384	0·3	9·6
3·6	0·0482	0·02	92	692	1	9·6
6·0	0·0482	0·02	92	1110	3	9·2

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[2] A. R. Martin and C. M. George, *J. Chem. Soc.*, 1933, 1413; A. Weissberger, 'Techniques of Organic Chemistry,' Interscience, New York, 1955, 2nd edn., vol. VII, p. 356; H. L. Rees and D. H. Anderson, *Analyt. Chem.*, 1949, **21**, 989

[3] V. Gold and J. H. Rolston, *J. Chem. Soc.* (*B*), 1970, 1795.

TABLE 4

Dependence of rate on concentration of potassium tetrachloroplatinate(II)

[NaCl] = 1·905 ± 0·005M

Expt. no.	[Pt(II)] / M	10^4[HCl] / M	w / Ci dm^{-3}	dA/dt / d.p.m. mol^{-1} s^{-1}	t_0 / h	$10^9\lambda$ / s^{-1}	Ratio
15	0·0201	92	3·6	663	3	9·19	2·1
16	0·0401	92	3·6	1361	4	18·9	
14	0·0198	10	4·0	941	4	11·7	2·5
19	0·0400	10	4·0	2310	5	28·8	
17	0·0201	0·92	3·6	1648	9	22·8	2·1
18	0·0401	0·92	3·6	3368	10	46·7	

TABLE 5

Dependence of rate on chloride concentration

[HCl] = 9·2 × 10^{-3}M

[NaCl] / M	dA/dt / d.p.m. mol^{-1} s^{-1}	t_0 / h	$10^9\lambda$ / s^{-1}	$10^9\lambda$[Cl$^-$] / M s^{-1}
0·97	3572	4	49·5	48·0
1·43	1908	7	26·4	37·8
1·90	1406	9	19·5	37·0

TABLE 6

Dependence of rate on concentration of hydrochloric acid

[NaCl] = 1·905 ± 0·005M

Expt. no.	[HCl] / M	dA/dt / d.p.m. mol^{-1} s^{-1}	t_0 / h	$10^9\lambda$ / s^{-1}
1	3 × 10^{-5}	2966	10	41·1
2	10^{-4}	3700	12	51·3
3	3 × 10^{-4}	2604	11	36·1
4	10^{-3}	1832	7	25·4
5	3 × 10^{-3}	1490	7	20·7
6	10^{-2}	1186	4	16·4
	10^{-2} *		~50	
7	3 × 10^{-2}	1092	3	15·1
8	10^{-1}	1082	4	15·0
9	10^{-6}	4460	13	61·8
10	10^{-5}	4088	12	56·7
11	10^{-4}	3270	10	45·3
12	10^{-3}	1900	7	26·3
13	10^{-2}	1240	6	17·2

* The solution in this experiment was identical in all respects with the preceding one, except that *ca.* 0·1 cm^3 of commercial hydrogen peroxide solution was added.

TABLE 7

Dependence of rate on concentration of added potassium hexachloroplatinate(IV)

w = 4·0 Ci dm^{-3}, [HCl] = 0·01M, [NaCl] = 1·41M

10^3[K$_2$PtCl$_6$] added / M	dA/dt / d.p.m. mol^{-1} s^{-1}	t_0 / h	$10^9\lambda$ / s^{-1}
0	1986	4	24·8
1·05	1804	30	22·5
2·07	1656	55	20·7
3·04	1620	81	20·2

not established in this work, but seems reasonable, on general grounds and in view of reports [4] that Pt^{II}-catalysed aromatic exchange reactions are sterically hindered at *ortho*-positions. In view of the induction period, the equation for the calculation of the first-order exchange rate constants was modified [equation (1)]. The time t_0 represents the induction period.

$$\lambda = [f/(t - t_0)]_{f\rightarrow 0} \qquad (1)$$

Oxidation of the side chain of benzyl alcohol samples from kinetic runs by alkaline permanganate (to benzoic acid) led to no significant reduction in the specific activity (Table 1), showing that our observations related exclusively to exchange in the aromatic ring.

Results of systematic kinetic experiments are given in Tables 2—7. Except where specified otherwise, these relate to a benzyl alcohol concentration of 0·0963M, a potassium tetrachloroplatinate(II) concentration of 0·04M, and a tritium activity (w) of 3·6 Ci dm^{-3}. All runs were performed at 50°. Values of induction periods (t_0) are tabulated but, except for the experiments on the systematic variation of the concentration of Pt^{IV} salt, the absolute magnitude of these times is not a reliable parameter.

DISCUSSION

The Induction Period and Inhibition by Platinum(IV).—Preliminary exchange studies had indicated an induction period of erratic nature and obscure origin as well as total inhibition of the exchange by low concentrations of potassium hexachloroplatinate(IV). More systematic work revealed the essential connection between these two phenomena. Addition of platinum(IV) salt causes a prolongation of the induction period to such an extent that no reaction at all is evident for several days. By extending the period during which measurements were taken, it was found that the dormant phase of the reaction eventually comes to an abrupt end and the exchange thereafter proceeds at a rate closely similar to that in the absence of added platinum(IV) salt (Figure 1). In the light of these observations it is easy to explain the erratic and much shorter induction period found without added platinum(IV) salt as being due to trace amounts of this salt as an impurity of variable amount in the platinum(II) salt used. It also becomes intelligible why there is an increase in the induction period as the concentration of tritiated water is raised (Table 2). Radiolytically produced hydrogen peroxide is known to be an impurity in tritiated water, which is not normally of significance. In our system this hydrogen peroxide can oxidise Pt^{II} to Pt^{IV} and thus produce the species responsible for the induction period, at a concentration which increases with the concentration of tritiated water used. The inference concerning the possible role of hydrogen peroxide was qualitatively confirmed (see Table 6).

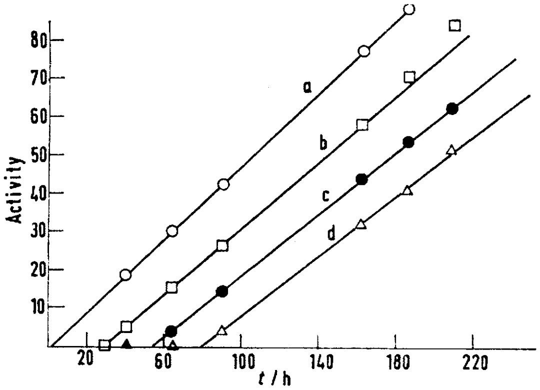

FIGURE 1 Effect of added potassium hexachloroplatinate(IV) on course of reaction: [added K$_2$PtCl$_6$] a, 0; b, 10^{-3}M; c, 2 × 10^{-3}M; d, 3 × 10^{-3}M. The activity plotted represents 10^{-3} × d.p.m. per 0·15 cm^3 sample counted. The filled triangle represents a superposition of an open triangle and a filled circle.

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

The resolution of the problem of the origin of the induction period was an essential step before other kinetic observations could be understood. In fact, the highly characteristic shape of the inhibition by platinum(IV) salt immediately leads to some quite general conclusions about the reaction mechanism and chemistry of the system. The observation that the exchange is almost totally suppressed during the initial phase and that this occurs at concentrations of platinum(IV) which are much lower than those of either platinum(II) or benzyl alcohol rules out the occurrence of some reactions (rapid or slow) of platinum(IV) with either one of these substances alone. If the binary interaction were to occur, the catalysed exchange reaction of benzyl alcohol, caused by interaction between unaffected platinum(II) salt and unaffected benzyl alcohol could still proceed, albeit at the slightly lower rate determined by the reduced concentrations of the two reactants. The oxidation product, benzaldehyde, is not implicated in the inhibition, since addition of that substance at a concentration of 3×10^{-3}M (equal to the highest concentration of Pt^{IV} in the experiments listed in Table 7) had no significant effect on the exchange reaction. The formation of traces of benzaldehyde during the exchange reaction is detectable by g.l.c., but the activity of the isolated benzyl alcohol is not due to it.

Only a mechanism of the general pattern of equation (A) is compatible with these findings. To account for

$$\begin{tikzcd}
PtCl_4^{2-} + PhCH_2OH \arrow[r, shift left, "k"] & X \arrow[l, shift left] \arrow[r, shift left, "k_{XY}"] \arrow[d, "+\,Pt^{IV}"] & \text{(exchange) } Y \arrow[l, shift left, "k_{XY}"] \\
 & Z & \\
 & \text{(benzaldehyde} + Pt^{II}\text{?)} &
\end{tikzcd}$$

(A)

the total inhibition during the induction period and the sharp break at its end we must conclude that reaction of X *with* Pt^{IV} is much more rapid than the further reaction of X which leads to exchange, so that no exchange can occur by this route as long as any Pt^{IV} remains in the system. The end of the induction period therefore corresponds to the complete reduction of platinum(IV) by a complex involving benzyl alcohol and platinum(II), after which the 'uninhibited' platinum(II) catalysis of benzyl alcohol exchange sets in. Alternatively it is conceivable that Z corresponds to a very stable Pt^{II}–Pt^{IV} complex which contains benzyl alcohol, implying irreversible removal also of some of the catalytically active platinum(II) species. This interpretation receives some support from the fact that the so-called 'uninhibited' reaction has a slightly lower rate in runs with added platinum(IV) salt (see final column of Table 7).

The small (not accurately determined) amount of exchange which occurs during the induction period must proceed by an alternative route, which is presumably identical with the mechanism for benzene exchange. Comparison of the results of the present work with those of the preceding paper indicates that under comparable conditions benzene exchange is *ca.* 40—50 times slower than exchange in benzyl alcohol.

It is further possible to show that formation of X must be the common rate-limiting process for both exchange and formation of Z. We envisage that the exchange reaction involves the formation of a further intermediate state Y, in which the entering tritium and leaving protium atoms occupy equivalent positions. The transformation from X to Y is rapid but may involve additional intermediate steps which are without kinetic significance. By analogy with the exchange mechanism for benzene [1] the change $X \longrightarrow Y$ is considered to be an associative reaction, *i.e.* the two equivalent hydrogen nuclei are held in a complex rather than as components of the solvent system. It follows that the rate of tritium uptake by benzyl alcohol (v_{ex}) will differ from the rate of the forward reaction forming X (v_+) by a kinetic isotope effect (called β in the preceding paper), or $v_{ex} = v_+\beta$. According to the interpretation of the Pt^{IV} inhibition given, v_+ is also equal to the rate of disappearance of Pt^{IV} from the solution, *i.e.* there are two ways of deriving the value of v_+ (or the related specific rate $k = v_+/[PhCH_2OH]$). From the steady exchange rate we have equation (2), and for the

$$k\beta = \lambda \qquad (2)$$

induction period equations (3)—(5) apply. Applying

$$-d[PtCl_6^{2-}]/dt = [PtCl_6^{2-}]_{t=0}/t_0 \qquad (3)$$

$$= k[PhCH_2OH] \qquad (4)$$

$$\therefore k = [PtCl_6^{2-}]_{t=0}/t_0[PhCH_2OH] \qquad (5)$$

equation (2) to the rate constant for the last experiment in Table 7, we calculate $k\beta = 2{\cdot}02 \times 10^{-8}\ s^{-1}$. Applying equation (5) to the induction period, we obtain $k = 3{\cdot}04 \times 10^{-3}/3600 \times 81 \times 0{\cdot}0963 = 10{\cdot}8 \times 10^{-8}\ s^{-1}$. The two calculations imply that the isotope effect β has a value of 0·19, which is reasonable for the mechanism considered, so that these results are entirely compatible with the statement of equation (A).

If we consider that $X \longrightarrow Y$ involves a proton (triton) transfer to X, then β is given by equation (6). The ratio

$$\beta = \frac{k_{XY}{}^{T}}{k_{XY}{}^{H}} \cdot \frac{k_{YX}{}^{H}}{k_{YX}{}^{H} + k_{YX}{}^{T}} \qquad (6)$$

$k_{XY}{}^{T}/k_{XY}{}^{H}$ measures the relative efficiency with which a triton rather than a proton is transferred to X. It is a 'product isotope effect' (in the sense in which that term has been used by us in analogous reactions [5]). If triton transfer occurs from an aqueous hydrogen ion, it may be looked upon as a product of a kinetic and a thermodynamic isotope effect. The latter expresses the relative abundance of tritium in hydrogen ions and water [5] (l_T) and the former the relative rate constants for triton and proton transfers, and their product would be expected to be of the order of [5] 0·1—0·2. The second factor on the right-hand side of equation (6) is expected to be of the order of 0·9—1, since the rate constant of the proton detachment reaction is expected to be at least ten times larger than the corresponding rate constant for triton

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[5] V. Gold and M. A. Kessick, *Proc. Chem. Soc.*, 1964, 295; *J. Chem. Soc.*, 1965, 6718.

detachment (for example from a cyclohexadienyl cation $ArHT^+$ in which the proton and triton considered occupy equivalent positions [6]).

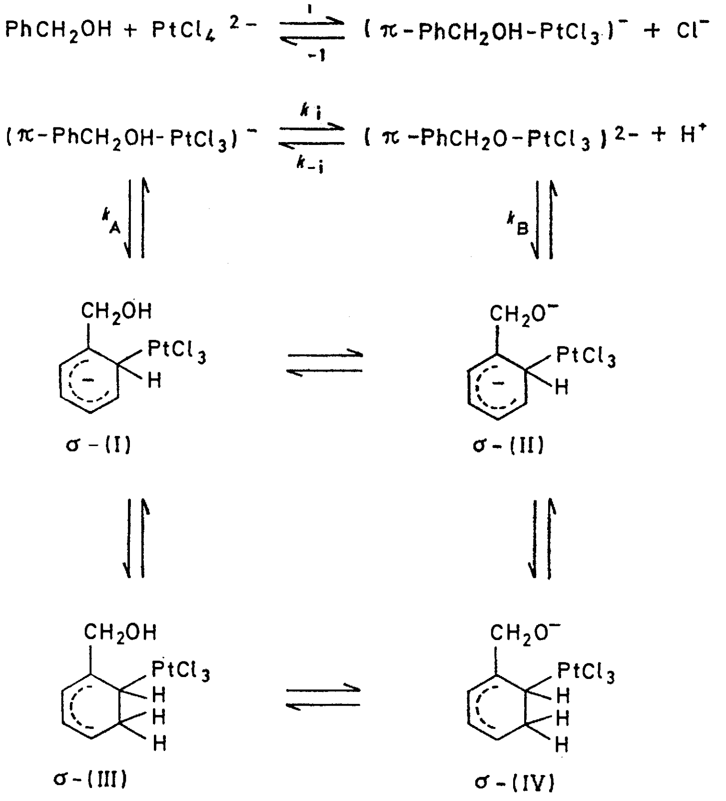
The Acidity-dependence of the Reaction.—The reaction was studied at several concentrations of added hydrochloric acid in the range 10^{-1}—10^{-6}M. At the low concentrations the solutions are largely unbuffered and the actual concentration of hydrogen ions is probably governed by hydrolysis of the tetrachloroplatinate(II) ion. At the highest concentrations of added acid the rate was found to be independent of hydrogen ion concentration and in the range 10^{-2}—10^{-4}M-hydrochloric acid the rate *increased* as the acidity fell off. This is in contrast to the results obtained with benzene.[1] At even lower concentrations the results become less reproducible, presumably because of the lower buffer capacity of the solutions, and the exchange rate constant appears to become slightly dependent on the concentration of benzyl alcohol in the solution. Because of the complexity of the catalyst system no attempt was made to control pH by use of some other buffer. The dependence of the exchange rate upon concentration of added hydrochloric acid appears to admit of two interpretations. According to the first, the rate levels off to a limiting value as the acidity is lowered, as suggested by the trend of experimental points in Figure 2, which is reminiscent of a titration curve with an inflection point about pH 3·5. Alternatively, it is possible that the rate continues to increase as pH increases but that the actual pH value of the solution (as distinct from −log [HCl] added) does not rise beyond 4—4·5 owing to hydrolysis of platinum(II) chloride species. On either interpretation there appear to be two exchange routes involving intermediates which are related as an acid–base pair, the more reactive being the basic form. The only difference between the two interpretations is the value to be assigned to the pK concerned. According to this model the acidity-dependence of the exchange rate constant should be expressed by equations (7) and (8) where $K_{IH} = [H^+][I^-]/[IH]$, and

$$k_+ = (k_A[IH] + k_B[I^-])/([IH] + [I^-]) \qquad (7)$$

$$= (k_A[H^+] + k_BK_{IH})/([H^+] + K_{IH}) \qquad (8)$$

where k_+ is the rate constant for the formation of the 'symmetrical' intermediate at the midpoint of the potential energy profile. Figure 2 includes some plots of equation (8) illustrating how adjustment of the parameters leads to curves corresponding to the two interpretations given above.

The increase of rate with decreasing acidity is in the opposite direction from the effect observed with benzene. The most apparent cause of the difference is the presence of the hydroxy-group of benzyl alcohol, and one may expect the acidity of this group to be markedly increased by co-ordination as work on the co-ordination of vinyl alcohol to platinum(II) suggests.[7]



$$PhCH_2OH + PtCl_4{}^{2-} \underset{-1}{\overset{1}{\rightleftharpoons}} (\pi\text{-}PhCH_2OH\text{-}PtCl_3)^- + Cl^- \qquad (9)$$

$$(\pi\text{-}PhCH_2OH\text{-}PtCl_3)^- \underset{k_{-i}}{\overset{k_i}{\rightleftharpoons}} (\pi\text{-}PhCH_2O\text{-}PtCl_3)^{2-} + H^+ \qquad (10)$$

(11)

(12)

This explanation does not by itself account for the apparent trend of induction periods to increase as the acidity is lowered, a trend in the opposite direction to the

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[6] B. D. Batts and V. Gold, *J. Chem. Soc.*, 1964, 4284; A. J. Kresge and Y. Chiang, *J. Amer. Chem. Soc.*, 1967, **89**, 4411.

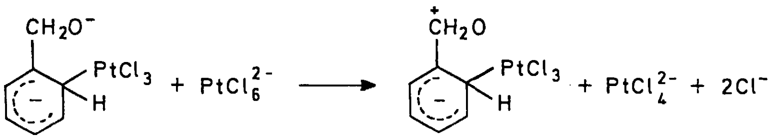
[7] M. Tsutsui, M. Ori, and J. Francis, *J. Amer. Chem. Soc.*, 1972, **94**, 1414.

expected inverse correlation between rate and induction period according to equations (2) and (5). This suggests that the mechanism in media of very low acidity may not conform to equation (A) or, alternatively, that the concentration of impurity Pt^{IV} in such media is increased by an oxidation reaction (by dissolved oxygen perhaps) which does not take place in acidic solution.

Reaction Mechanism.—The foregoing formal deductions about the mechanism can be incorporated in a chemically explicit mechanism formulated by analogy with the mechanisms considered by us for benzene.[1] If the protolytic equilibria are mobile and the steps denoted by k_A and k_B [*cf.* equations (7) and (8)] are rate limiting in the formation of the midpoint intermediates given in equation (12), then the rate constant for the formation of these intermediates (the total, in both forms) will be given by equation (13) where $K = k_i/k_{-i}$. Equation (13)

$$k_+ = \frac{k_1[PtCl_4^{2-}]}{k_{-1}[Cl^-]}\left\{\frac{k_A[H^+] + k_BK}{[H^+] + K}\right\} \qquad (13)$$

shows the dependence on Pt^{II} and chloride concentration required by the results and it expresses the acidity-dependence in the same form as equation (8). Equation (13) is analogous to equation (10) of the preceding paper in that it assumes that the ring protonation of the first σ-complex occurs rapidly. The formation of σ-(III) and σ-(IV) from their respective precursors σ-(I) and σ-(II), the rate of which would be expected to depend on hydrogen ion concentration, therefore does not come into the kinetic expression. In the case of benzene the corresponding levelling-off of the acidity dependence occurred only at high acid concentrations, whereas it is here assumed that the rearrangement from π- to σ-complex is also rate limiting at low acidities. The higher reactivity of the complex σ-(II) towards ring protonation compared with the benzene analogue, combined with the possibility that the π–σ rearrangement may be slower for benzyl alcohol, could account for this difference in behaviour.



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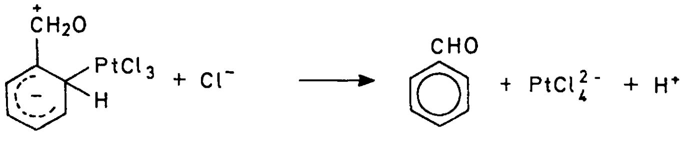


(15)

We must note here that this representation of the mechanism does not allow us to envisage the effect of the $PtCl_3^-$ group on the aromatic ligand as being expressed as simple electron withdrawal from or electron donation to the ring. On the one hand, we have to assume that the $PtCl_3^-$ group enhances the acidity of the side chain hydroxy-group which implies electron withdrawal (and is analogous to the previously quoted acid-strengthening of a vinyl alcohol ligand). On the other hand, the co-ordination must render the ligand group more reactive towards ring protonation (and this is illustrated without the complications of protolytic equilibria in the case of benzene exchange). It may not be too fanciful to suggest that the acid-strengthening corresponds to the normal inductive 'through-bonds' withdrawal by the co-ordinated metal, whereas the π-back-donation affects the adjoining π-system but is not relayed through the methylene group of the side chain.

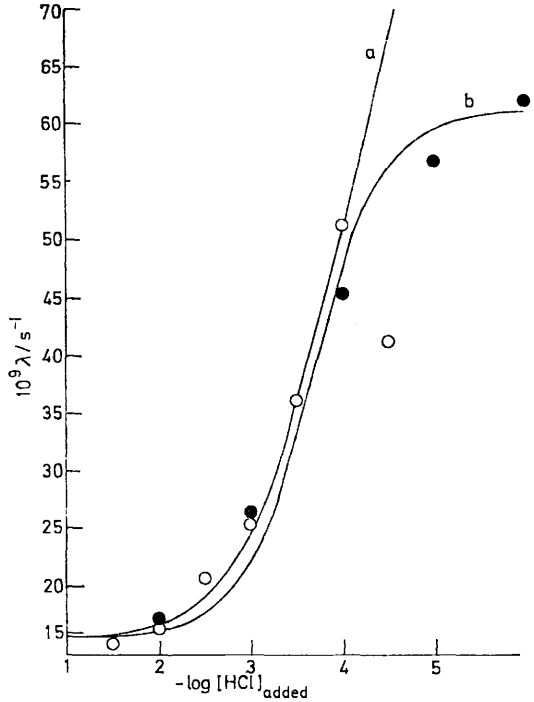
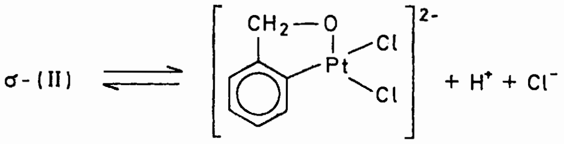


FIGURE 2 Acidity-dependence of λ: the curves are representations of equation (8), with *a*, $k_a = 15{\cdot}5$, $k_b = 83{\cdot}2\ s^{-1}$, $K_{IH} = 2{\cdot}5 \times 10^{-4}M$ and *b*, $k_a = 15{\cdot}5$, $k_b = 61{\cdot}0\ s^{-1}$, $K_{IH} = 1{\cdot}0 \times 10^{-4}M$; filled circles are points for experiments 9—13 in Table 6; open circles for experiments 1—7)

The pair of complexes σ-(I) and σ-(II) corresponds to the intermediate X of equation (A), the reaction of which with platinum(IV) is responsible for the induction period. We consider this reaction to be initiated by a (possibly stepwise) two-electron transfer according to equation (14), followed by decomposition of the oxidised complex of benzaldehyde. [Alternatively the oxidation could involve σ-(III) and σ-(IV)]. This is expressed stoicheiometrically in equation (15). This scheme is of the same overall stoicheiometry as the oxidation of pyridylmethanols to the corresponding aldehydes by Ce^{IV}, a reaction which is greatly accelerated[8] by co-ordination of the pyridylmethanol to cobalt(III).

A further possibility, mentioned on p. 1876, is that the product of reaction (14) is a stable Pt^{II}–Pt^{IV}–benzyl alcohol complex. This complex can be an intermediate in the oxidation process as the formation of benzaldehyde may possibly take place during the sample isolation.

Since the steps of the exchange mechanism subsequent to the formation of σ-(I) $\rightleftharpoons$ σ-(II) are not rate limiting, one is free to speculate about possibly more attractive alternatives for them, such as the scheme in equation (16). This would confine exchange to *ortho*-positions, a point not so far investigated. However, we are at present unable to distinguish this and similar alternatives, and we shall therefore not extend these speculations.



(16)

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[8] J. E. French and H. Taube, *J. Amer. Chem. Soc.*, 1969, **91**, 6951.