Pt(II) COMPLEXES
IN ACTIVATION OF SATURATED HYDROCARBONS

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The rate constants of deuterium exchange for cyclohexane in CH_3COOD/D_2O have been measured in the presence of 12 complexes of Pt(II) with various ligands (Cl, H_2O, NH_3, Br, NO_2, py, DMSO, PPh_3, etc.). The change in the rate constant is shown to follow the reverse series of the trans-effect of Pt(II) ligands. The rate constant of the interaction of $PtCl_2S_n$ (S is H_2O, CH_3COOH, n = 1, 2) with cyclohexane in CH_3COOD/D_2O (1:1), k, equals 2.5×10^8 exp (−18200/RT) l $mol^{-1}sec^{-1}$ (at 354 − 385 K). The ratio of rate constants for $PtCl_2S_2$, $PtCl_3S^-$ and $PtCl_4^{2-}$ is 100 : 6 : 0.5 at $100°C$.

Измерены константы скорости дейтерообмена циклогексана в среде $CH_3COOD-D_2O$ при катализе 12-ю комплексами Pt(II) с различными лигандами (Cl, H_2O, NH_3, Br, NO_2, py, DMCO, PPh_3 и др.). Показано, что изменение константы скорости следует обратному ряду трансэффекта лигандов у Pt(II). Для комплекса $PtCl_2S_n$ (S − H_2O, CH_3COOH, n = 1,2) константа скорости взаимодействия его с циклогексаном в 1:1 $CH_3COOD - D_2O$ k = $2,5 \cdot 10^8$ exp(−18200/RT)л. моль$^{-1}$сек$^{-1}$ (354-385 °К). Константы скорости при $100°C$ для $PtCl_2S_2$, $PtCl_3S^-$ и $PtCl_4^{2-}$ относятся между собой как 100:6:0,5.

At 80 − $120°C$ in aqueous media saturated hydrocarbons undergo deuterium exchange reactions, oxidative halogenation, and dehydrogenation in the presence of chloroplatinum complexes of /1, 2/. As demonstrated /3, 4/, the direct interaction of the hydrocarbon with the Pt(II) complex, resulting in the formation of a Pt−C bond, i. e. the activation of the hydrocarbon towards various reactions, is the limiting stage of these processes. Further elucidation of the nature of this interaction requires studies of the effect of ligands on the catalytic properties of Pt(II) complexes. In the

present work deuterium exchange with cyclohexane catalyzed by $PtCl_3^-$ (L = H_2O, Cl^-, NO_2^-, DMSO, NH_3, py), $PtCl_2L_2$ (L = H_2O, Cl^-, Br^-, I^-, NO_2^-, CN^-, PPh_3) and other complexes has been studied. The complexes were synthesized by known methods; the rate constants were measured for analytical grade samples. The experiments were conducted in evacuated glass ampoules at a liquid/gas phase ratio of 4 : 1 (20^oC) and at [RH] = 0. 15 M. The constants found under these conditions are shown to correspond, within the experimental error, to those measured in the absence of a gas phase. Mass spectra of deuterocyclohexanes were measured on a MI-1305 spectrometer with a SI−03 attachment at an ionizing voltage of 16 eV. The experimental value of the rate constant was determined as the average of 3 − 5 measurements, using the formula

$$k = \Sigma' d_i t^{-1} [Pt^{II}]^{-1} \text{ 1 mol}^{-1} \text{sec}^{-1}$$

where $\Sigma' d_i$ is the fraction of cyclohexane molecules[1] involved in deuterium exchange.

As follows from Table 1, the rate constant of deuterium exchange, depending on the ligand, varies over three orders of magnitude, decreasing for more basic and softer, easily polarizable ligands with a stronger tendency, to double bonding. Table 2 gives the rate constants for catalysis by complexes formed in the system

$$PtCl_2S_2 + 2X^- \rightleftharpoons PtCl_2X_2 + 2S.$$
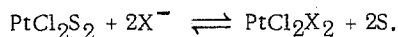
The decreasing exchange rate in the series X = F > Cl > Br > I > NO_2 corresponds to the behavior of $pK_{PtX_4^{2-}}$ (see Fig. 1) /5/, to the overlap integral of Pt 6p σ orbitals and ligand pσ orbitals /6/ as well as to the parameters of ligand softness or hardness (σ_X) /7/. A ligand may evidently affect both the degree of PtX_2 complex formation in solution and the electronic properties of the complex as a whole. The strong influence of a ligand on the electronic properties of a catalytically active species is

Table 1

Deuterium exchange of cyclohexane in the presence of Pt(II) complexes

$[Pt] = 0.0043$ M $(1 - 2)$; 0.02 M $(3 - 12)$; $[HClO_4] = 0.1$ M;

$[C_6H_{12}] = 0.15$ M; 100°C

No.	Complex	Time (hrs)	Σd_i	$k \times 10^3$ (l mol^{-1} sec^{-1})	$M = \dfrac{\Sigma i d_i}{\Sigma d_i}$
1	$PtCl_2S_2$	2	0.230	7.42	1.93
2	$KPtCl_3S$	2	0.154	4.97	1.74
3	K_2PtCl_4	1.66	0.333	2.78	1.75
4	$K_2Pt(NO_2)Cl_3$	7	0.185	0.366	1.52
5	$KPt(NH_3)Cl_3$	2.5	0.140	0.777	1.65
6	$KPt(py)Cl_3$	12	0.0268	0.025	1.46
7	$KPt(DMSO)Cl_3$	12.5	0.0549	0.056	1.60
8	$Pt(DMSO)Cl(NO_3)$	4	0.0242	0.083	1.62
9	$K_2Pt(NO_2Cl)_2$	7	0.0584	0.115	1.41
10	$Pt(PPh_3)_2Cl_2$	16.5	0.0078	0.007	1.34
11	$Pt(acac)_2$	7.5	0.0511	0.094	1.57
12*	$Pt(CF_3COO)_2$	0.3	0.0158	0.732	1.34

*Experiment carried out in CF$_3$COOD at 91°C

revealed by comparing $[PtCl_3L]^-$ type complexes where L = Cl^-, H_2O, NH_3, DMSO. The instability constants of aqua and DMSO complexes are close to each other, i. e. the concentrations of active complexes $PtCl_2(DMSO)S$ and $PtCl_2(H_2O)S$ in solution are almost the same, but the rate constants of deuterium exchange catalyzed by these complexes differ by more than one order of magnitude. The introduction of dimethyl

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Table 2

Effect of anions on deuterium exchange of cyclohexane

in the presence of $PtCl_2S_2$

$[Pt^{II}] = 0.0043$ M; $[X^-] = 0.0086$ M; $[HClO_4] = 0.1$ M; [pyrene] $= 0.031$ M;

$[C_6H_{12}] = 0.15$ M

X	–	CF_3COO	F	$1/2SO_4$	Cl	Br	I	NO_2	CN
$k \times 10^3$, (1 $mol^{-1}sec^{-1}$)	6.30	6.28	6.26	6.06	4.10	2.47	0.394	0.115	0.106
σ_X	13.05		12.18		9.92	9.22	8.31	5.87	
M	2.02	1.94	1.92	1.98	1.77	1.48	1.52	1.42	1.52

sulfoxide, a strong π-acceptor, increases the positive charge on the central ion,

which, in accordance with the donor nature of the hydrocarbon, should accelerate

deuterium exchange (similarly to the effect observed in the series $H_2O > NH_3$). The

observed decrease in the exchange rate is due to an increasing softness (increased

double bonding) upon going in the series of ligands from oxygen to sulfur (or, similar-

ly, from nitrogen to phosphorus). Indeed, the values of oxidation numbers in

$Pt(C_2H_4)Cl_3^-$ and $Pt(H_2O)Cl_3^-$ (ethylene and DMSO are close in their acceptor prop-

erties) are 2.9 and 2.44, respectively /8/. The increasing oxidation number of the

metal in the complex reduces the ability of the complexes to oxidative addition of

alkanes. It is well known that soft ligands stabilize Pt(II) complexes with respect to

transition into Pt(IV). The rate of deuterium exchange with cyclohexane increases

in the order of ligands: CN $\sim$ CNS $<$ PPh$_3$ $<$ DMSO $\sim$ py $<$ NO$_2$ $<$ I $<$ Br $<$ NH$_3$ $<$

Cl $<$ H$_2$O $\sim$ F $\sim$ SO$_4$. This corresponds to the reverse order of the trans-effect of

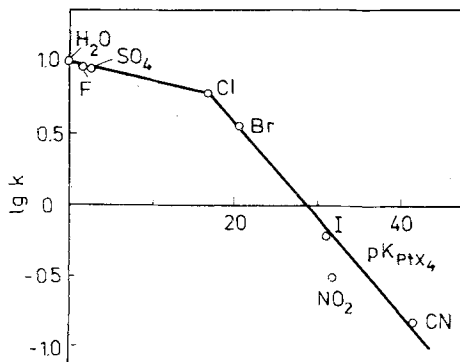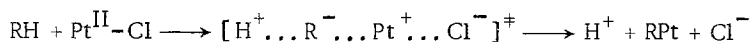ligands in substitution reactions of square planar Pt(II) complexes /6/. Thus, the

Fig. 1.

result obtained is not consistent with the direct substitution of a Pt(II) ligand by a hydrocarbon:

$$RH + Pt^{II}-Cl \longrightarrow [H^+ \ldots R^- \ldots Pt^+ \ldots Cl^-]^{\ddagger} \longrightarrow H^+ + RPt + Cl^-$$

which is similar to the mechanism of substitution in square planar complexes of platinum and, hence, should have corresponded to a normal series of the trans-effect. On the other hand, the inversed series of the trans-effect of ligands is, in our opinion, in accordance with the homolytic cleavage of RH by a Pt(II) complex, resulting in the formation of Pt–H and Pt–R bonds. Indeed, the logarithm of the rate constant for the homolytic detachment of H and R by an active species is linearly related to the strength of the bond arising between this species and H or R /9/: $\log k = a + bD$ (PtH or PtR). As shown /10/, the frequency of the Pt–C bond, and hence its strength, in trans-Pt $(CH_3)X(PEt_3)_2$ decreases in the series X = NO_3, NCS $\gg$ Cl $>$ Br $>$ NO_2 $>$ I $>$ CN, which is an inversed trans-effect series. The frequency of the Pt–H bond and its strength in PtA_2LH fall in a similar series: L = $NO_3 >$ Cl $>$ I $>$ NO_2 $>$ SCN $>$ CN /11/.

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Thus, the rate constant of exchange should in general be dependent on the degree of PtX_2 complex formation[*], determining the concentration of free PtX_2 in solution, and on the nature of ligands in PtX_2 manifesting itself in the value of k_1, the rate constant for uncomplexed PtX_2. Taking into consideration that in the series PtX_2, PtX_3^-, PtX_4^{2-} the complex PtX_2 is the most active, the following relationship may be written as a first approximation: $k = k_1 [PtX_2]_0 / \Phi$, where Φ is a function of the degree of complex formation between PtX_2 and a ligand in solution. For chloro complexes of platinum

$$k = \frac{(k_1 + k_2 K_2 [Cl^-] + k_3 K_{12} [Cl^-]^2) [PtCl_2]_0}{1 + K_2 [Cl^-] + K_{12} [Cl^-]^2}$$

and from the relationship between k and $[Cl^-]$ the partial constants k_1, k_2, and k_3 can be evaluated for the complexes $PtCl_2S_2$, $PtCl_3S^-$, and $PtCl_4^{2-}$, which are at equilibrium in solution; K_1 and $K_{12} = K_1 K_2$ are the constants of these equilibria. We have found that $k_1 : k_2 : k_3 = 100 : 6 : 0.5$ at $100^\circ C$. For exchange with the participation of $PtCl_2S_2$ the temperature dependence of the rate constant in the range from 81 to $112^\circ c$ was measured (Fig. 2). It was found that $k_1 = 2.5 \times 10^8 \exp (18200/RT)$ l $mol^{-1} sec^{-1}$. The activation parameters, $\Delta H^{\ddagger} = 17.5$ kcal mol^{-1}, $\Delta S^{\ddagger} = -22.6$ e.u. can be compared with the respective parameters for the process of H_2 binding by the complex $IrCl(CO)(PPh_3)_2$ /13/:

$$\Delta H^{\ddagger} = 10 - 13 \text{ kcal mol}^{-1}, \quad \Delta S^{\ddagger} = -(14 - 24) \text{ e.u.}$$

[*]Further solvolysis of PtX_2 should be a much slower process /12/ and does not substantially contribute to the equilibria of Pt(II) complexes in solution at not very small $[Pt^{II}]$.

Fig. 2.

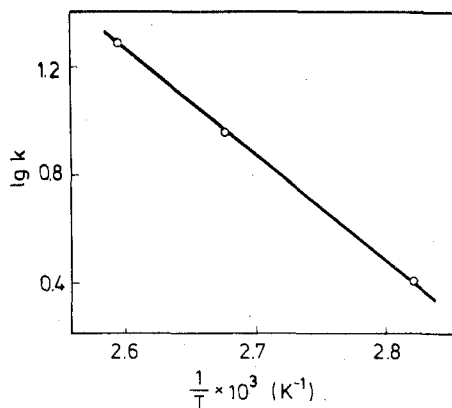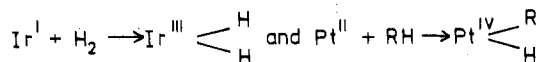The close values of $\Delta S^{\ddagger}$ are in agreement with a common mechanism for both processes:

$$Ir^{I} + H_2 \longrightarrow Ir^{III} \diagdown\diagup_{H}^{H} \quad \text{and} \quad Pt^{II} + RH \longrightarrow Pt^{IV} \diagdown\diagup_{H}^{R}$$

Thus, the results of the present work unambiguously confirm the previous assumption /3/ that the interaction of alkanes with platinum follows the mechanism of oxidative addition.

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