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KINETICS AND MECHANISM OF THE DECOMPOSITION OF $Cs_2Pt[CH_3]_2Cl_4$ IN AQUEOUS SOLUTION WITH CONCURRENT FORMATION OF C_2H_6, C_2H_4, AND C_2H_5Cl

V. V. Zamashchikov and V. G. Popov

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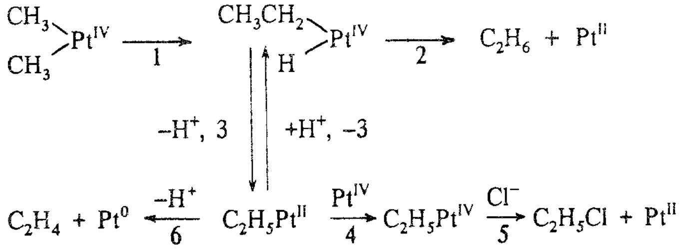
Reductive elimination of ethane from $Cs_2Pt(CH_3)_2Cl_4$ in aqueous chloride solutions at 368 K is accompanied by C–H bond scission. A mechanism is proposed for the reaction which includes the intermediate formation of an ethylhydrideplatinum(IV) and an ethylplatinum(II) complex.

Reductive elimination leading to the formation of a C-C bond is an important, but little studied, reaction of organic derivatives of the transition metals; such reactions are frequently terminal stages in homogeneous catalytic processes (see [1]). For model systems – polymethyl d^6 complexes of platinum and palladium – reductive elimination of ethane is considered as the result of concerted scission of two metal-carbon bonds with the formation of a C-C bond [2, 3].

We observed that decomposition of the dimethyl complex $Cs_2Pt(CH_3)_2Cl_4$, synthesized by a known method [4], in D_2O-DCl solution (3.0 mole/liter) at 368 K gave a mixture of $C_2H_{6-i}D_i$ in the ratio 1.0:0.8:2.0:2.2:0.2:0.3:0.3 for $i = 0$ to 6 respectively. (It was earlier thought [5] that dimethylplatinum (IV) complexes underwent only substitution of ligands without Pt–C bond scission in aqueous solution.) Since deuterium exchange via secondary reactions of ethane with platinum (II) under these conditions can be ruled out (see [6]) and since, according to ^1H NMR results, $[Pt^{IV}(CH_3)_2]^{2+}$ complexes do not undergo H/D exchange with the medium, this result indicates C–H bond scission before separation of ethane. Consequently the concerted mechanism for ethane formation is excluded in our case.

The following scheme is proposed based on the experimental results:



(1)

The basis for this scheme is as follows. The rate constant for ethane evolution

$$k_{EtH} = \frac{1}{[Pt^{IV}(CH_3)_2]_0}\left(\frac{d[C_2H_6]}{d\tau}\right)_{\tau\to 0},$$

were measured by a GLC method. It did not depend on $[Pt^{IV}(CH_3)_2]_0$ in the range $1.0\cdot10^{-3}$ to $7.3\cdot10^{-3}$ mole/liter in the system $Cs_2Pt(CH_3)_2Cl_4$ (10^{-3} mole/liter)–HCl–NaCl–H_2O ($[Cl^-] = 3.0$ mole/liter, 368 K) (system I). The values of k_{EtH} remained practically constant with $[H^+]$ from 0.01 to 3.0 mole/liter (see Table 1). However as a result of concurrent protolysis (stage −3) and oxidation (4) of the ethyl complex $C_2H_5Pt^{II}$ on addition of Na_2PtCl_6 (see [7]) the yield of ethane was reduced and ethyl chloride was evolved. The latter was formed by S_N2 decomposition of ethylplatinum(IV), the oxidation product of

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L. M. Litvinenko Institute of Physico-organic and Coal Chemistry, Academy of Sciences of Ukraine, Donetsk. Translated from Teoreticheskaya i Éksperimental'naya Khimiya, Vol. 29, No. 2, pp. 154-158, March-April, 1993. Original article submitted June 4, 1993 [sic].

TABLE 1. Rate Constants for the Evolution of Ethane and Ethene in Systems I and II (system compositions are discussed in the text)

Parameter	I	II				
$[H^+]$, mole/liter	$\sim 10^{-7}$	0,01	0,026	0,262	0,533	3,0
$k_{EtH}\cdot 10^7$, s^{-1}	0,16	1,79	1,76	1,94	2,13	2,35
$k_{en}\cdot 10^7$, s^{-1}	1,6	0	0	0	0	0

TABLE 2. Dependence of the Rate Constant for the Evolution of Ethane in System I on the Acidity of the Medium and the Addition of Na_2PtCl_6.

$[H^+]\cdot 10$, mole/liter	$[Pt^{IV}]\cdot 10^2$, mole/liter	$[Pt^{IV}]/[H^+]\cdot 10$	$k_{EtH}\cdot 10^8$, s^{-1}	$k^*_{EtH}\cdot 10^8$, s^{-1}
2,62	0	0	19,4	19,3
7,50	3,3	0,446	10,5	11,3
2,62	2,78	1,06	7,94	7,65
2,62	5,69	2,17	5,30	5,31
2,62	11,9	4,56	3,74	3,74
0,655	4,36	7,79	2,52	3,06
0,655	4,81	18,4	1,97	2,46
0,147	4,27	29,0	1,98	2,29

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*Calculated from Eq. (2).

$C_2H_5Pt^{II}$ (stage 5). In agreement with scheme (1), the sum of the values of k_{EtH} and the rate constant for the evolution of ethyl chloride, k_{EtCl}, measured analogously, remains constant:

$[Pt^{IV}]/[H^+]$	$k_{EtH}\cdot 10^7$, s^{-1}	$k_{EtCl}\cdot 10^7$, s^{-1}	$(k_{EtH} + k_{EtCl})\cdot 10^7$, s^{-1}
0	2,3 ± 0,1	0	2,3 ± 0,1
2,0	0,20 ± 0,01	2,2 ± 0,2	2,4 ± 0,2

and the value of k_{EtH} is independent of $[Pt^{IV}]$ with a constant ratio $[Pt^{IV}]/[H^+] = 0.78$:

$[Pt^{IV}]\cdot 10^2$, mole/liter	1,15	4,50	10,2	20,4	
$k_{EtH}\cdot 10^8$, s^{-1}	2,2	2,3	2,1	2,4	2,2±0,1 (av)

Increasing the ratio $[Pt^{IV}]/[H^+]$ led to a decrease in the value of k_{EtH} (Table 2) according to the expression

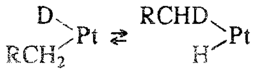
$$k_{EtH} = \frac{1 + (2{,}0 \pm 0{,}3)[Pt^{IV}]/[H^+]}{(5{,}2 \pm 0{,}9)\cdot 10^6 + (1{,}01 \pm 0{,}08)\cdot 10^8 \cdot [Pt^{IV}]/[H^+]}, \qquad (2)$$

which agrees with scheme (1). From the parameters of this equation we found $k_1 = (1.9 \pm 0.3)\cdot 10^{-7}\ s^{-1}$; $k_4/k_{-3} = 2.0 \pm 0.3$; $k_2/k_3 = 0.10 \pm 0.04$, where k_i is the rate constant for the corresponding stage. Expression (2) reaches a plateau with $[Pt^{IV}]/[H^+] \geq 1.8$ which corresponds to conditions in which the intermediate $C_2H_5Pt^{II}$ is practically completely intercepted by the oxidizing agent.

On changing from acid to neutral conditions (system II, $Cs_2Pt(CH_3)_2Cl_4$ (10^{-3} mole/liter)$-$NaCl (3.0 mole/liter)$-$$Na_2HPO_4-KH_2PO_4-H_2O$, pH $\approx$ 7 (phosphate buffer), 368 K), stage -3 decelerates because of the decrease in $[H^+]$ and, in the absence of an oxidizing agent route 6, the decomposition of ethylplatinum(II) to give ethene, takes over. Similar reactions are known for dialkyl d^8 complexes of platinum [1]. The rate constant for the evolution of ethene, k_{en}, measured analogously to k_{EtH}, is also independent of $[Pt^{IV}(CH_3)_2]_0$. The sum $k_{en} + k_{EtH}$ is practically the same (Table 1) as the value of k_{EtH} in system I where $C_2H_5Pt^{II}$ is intercepted by H^+ in the absence of an oxidizing agent. Addition of Na_2PtCl_6 (0.01 to 0.04 mole/liter) to system II completely inhibits the formation of ethene and diverts ethylplatinum(II) to the concurrent stage 4.

The decomposition of $[Pt^{IV}(CH_3)_2]^{2+}$ in system II gave ethane as well as ethene (Table 1) and addition of Na_2PtCl_6 had practically no effect on the rate of ethane evolution ($k_{EtH} = (2.3 \pm 0.6)\cdot 10^{-8}$ s^{-1} with $[Pt^{IV}] = 0$ to 0.04 mole/liter). We emphasize that, according to scheme (1), the formation of ethane under these conditions does not involve steps 3 and -3. Consequently the values of k_{EtH} obtained coincide with the value of $k_{EtH} = 2.0\cdot 10^{-8}$ s^{-1} in system I with $[Pt^{IV}]/[H^+] \geq 1.8$ when the same "shortened" route for ethane evolution occurs.

The first kinetically significant intermediate in scheme (1) is the ethylhydride complex of platinum(IV). The reversible elimination of H^+ from this complex (step 3) leads to the formation of an ethyl complex of platinum(II), while step (2) gives ethane (see [6]). Introduction of the complex $C_2H_5Pt^{IV}H$ into scheme (1) provides an explanation for the evolution of ethane-d_1 during the decomposition of $Cs_2Pt(CH_3)_2Cl_4$ in a medium containing D^+. It is known that similar alkyl hydride d^6 complexes of Rh and Ir are able to rearrange [8]:



$$\begin{matrix} D \\ RCH_2 \end{matrix} > Pt \rightleftarrows \begin{matrix} RCHD \\ H \end{matrix} > Pt$$

We note that the formation of $C_2H_5Pt^{IV}H$ from $[Pt^{IV}(CH_3)_2]^{2+}$ may occur via an intermediate carbene complex of platinum(IV). Such a route has been discussed [3] as one variant for the decomposition of trimethylpalladium(IV), an analog of $[Pt^{IV}(CH_3)_2]^{2+}$.

It is natural to ask why the dimethyl complex "chooses" the complex path, including steps 1 and 2, to eliminate ethane. According to the results of quantum chemical calculations on the decomposition of $Pt^{II}(CH_3)_2$ and $Pd^{II}(CH_3)_2$ by direct interaction of two sp^3 centers (methyl ligands) in a concerted reaction to evolve ethane corresponds to a very high energy barrier. This makes a multistage reductive elimination mechanism preferable.

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