

Kinetics and Mechanism of the Reductive Elimination of Oxiranes from “Platinahydrins” (Platinum β -Hydroxyethyl Complexes)

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Abstract—The β -hydroxyethyl platinum(IV) derivatives with the general formula $[\text{Cl}_3\text{Pt}^{\text{IV}}-\text{CH}_2\text{CH}(\text{OH})\text{R}]^{2-}$, where R = H (**1**) or CH_2Cl (**2**), are fairly stable in aqueous solution at pH < 7. In neutral and weakly alkaline solutions, they decompose, yielding the corresponding epoxide $\text{CH}_2(\text{O})\text{CHR}$ and the PtCl_4^{2-} anion. This decomposition takes place via reductive elimination caused by an intramolecular nucleophilic attack of the oxygen atom on the α -carbon atom of “platinahydrin” **1** or **2**.

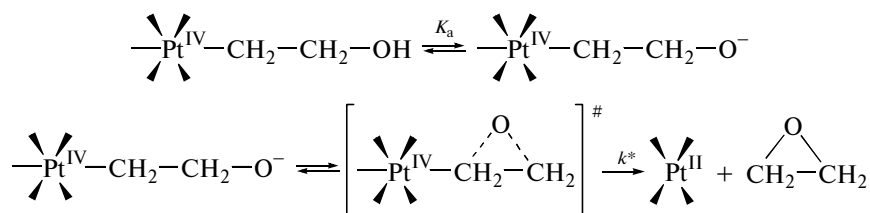
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β -Hydroxyalkyl derivatives with the general formula $\text{L}_n-\text{M}-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_2-\text{R}$ are key intermediates in a number of important catalytic processes [1], including the well-known olefin oxidation reaction catalyzed by palladium(II) [2, 3]. Also known are fairly stable representatives of this class of organometallic compounds, for example, $\text{L}-\text{Hg}-\text{CH}_2-\text{CH}(\text{OH})\text{CH}_2\text{R}$ [4].

The β -hydroxyalkyl platinahydrins synthesized by us, $\text{L}_5-\text{Pt}(\text{IV})-\text{CH}_2-\text{CH}(\text{OH})\text{CH}_2\text{R}$ [5], are intermediate in reactivity. They are sufficiently stable to be isolated and to study their spectral and other properties. At the same time, they readily undergo chemical conversions, such as reductive elimination yielding

fragments of the organic moiety of the platinahydrin and a platinum(II) complex. This makes them convenient objects for investigating the kinetics and mechanism of particular stages of catalytic reactions.

For the first time, the formation of the simplest platinahydrin $\text{Pt}(\text{IV})-\text{CH}_2-\text{CH}_2-\text{OH}$ in aqueous solutions was observed in the oxidation of Zeise's salt anion $\text{Cl}_3\text{Pt}(\text{CH}_2=\text{CH}_2)^-$ with molecular chlorine [6]. It was noted that alkalifying the platinahydrin solution yields ethylene oxide. The mechanism of this process was not discussed in that work [6], but now it can be hypothesized that ethylene oxide resulted from reductive elimination through intramolecular attack by the alkoxide ion on the α -carbon atom.



Scheme 1.

Preliminary kinetic data [5] demonstrated that the regularities of the decomposition of an analogue of the compound $\text{Cl}_5-\text{Pt}(\text{IV})-\text{CH}_2-\text{CH}_2-\text{OH}$ (**1**), namely, the complex $\text{PtCl}_5(\text{CH}_2\text{CHOHCH}_2\text{Cl})^{2-}$ (**2**) obtained by the oxidative addition of epichlorohydrin to PtCl_4^{2-} , differ from the regularities of reductive elimination for most platinum(IV) alkyl chloride complexes: alkalify-

ing the solution yields epichlorohydrin, reductive elimination is slowed down by Cl^- admixtures, and the apparent rate constant of the decomposition of **2** increase with increasing pH. These observations are consistent with the intramolecular mechanism of reductive elimination (Scheme 1). A similar mechanism was suggested in a recent work [7] for the decom-

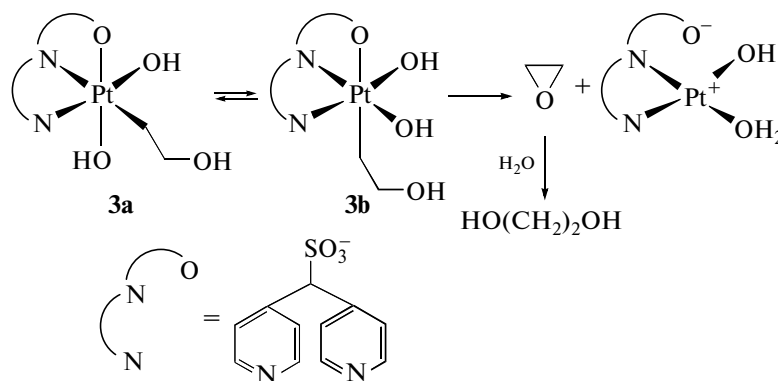
position of the platinahydrin $L\text{-Pt}^{\text{IV}}(\text{OH})_2(\text{CH}_2\text{-CH}_2\text{-OH})$ (Scheme 2). The half-life of the initial unsymmetrical platinahydrin **3a** (according to the terminology of Khusnutdinova et al. [7]) is approximately 1 h at 80°C . Oxirane formation begins only after the isomerization of **3a** into symmetrical complex **3b**, which has a weakly bound sulfo group oxygen atom *trans* to the hydrin fragment. The resulting oxirane hydrolyzes rapidly into ethylene glycol (Scheme 2).

The first detailed kinetic study of the decomposition of the platinahydrin $\text{Cl}_5\text{-Pt}(\text{IV})\text{-CH}_2\text{-CH}_2\text{-OH}$ (**1**), carried out by Luinstra et al. [8], demonstrated that compound **1** in aqueous solutions

($[\text{KCl}] + [\text{KNO}_3] = 3.0 \text{ mol/l}$) at 60°C undergoes reductive elimination yielding a mixture of ethylene glycol and chloroethanol. The yield of the latter increases with increasing $[\text{Cl}^-]$. The authors of that study believed that the reductive elimination mechanism in this case is the same as in the reactions of the other known monoalkyl derivatives of platinum(IV). Specifically, an $\text{S}_{\text{N}}2$ attack of the external nucleophile on the α -carbon atom of the substrate takes place:

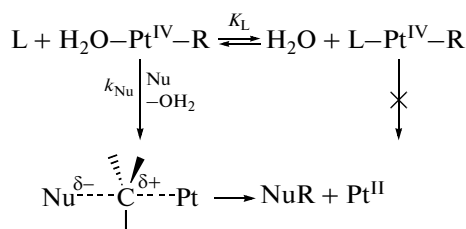


($\text{Nu} = \text{Cl}^-$, Br^- , I^- [9], SCN^- , $\text{S}_2\text{O}_3^{2-}$ [10], PtCl_4^{2-} [11] and H_2O [9]; $\text{X} = \text{Cl}$ or Br ; $\text{R} = \text{CH}_3$, C_2H_5 , CH_2COOH , CH_2COCH_3 , $\text{CH}_2\text{CH}_2\text{NH}_3^+$).



Scheme 2.

The platinum(II) complex in these reactions is a leaving group. It differs from “ordinary” (non-metal-complex) leaving groups in that the breaking of the platinum–carbon bond is accompanied by the breaking of the bond between the platinum atom and the ligand *trans* to the alkyl group of the initial complex. Thus, at given Nu and R, the reactivity of platinum alkyl complexes in reaction (1) is determined by the strength of the Pt–L bond. In this class of reductive elimination reactions, nearly all of the reactions studied to date proceed at a noticeable rate only when the *trans* position to the alkyl group is occupied by an aqua ligand ($\text{L} = \text{H}_2\text{O}$, Scheme 3). Replacing this ligand with a group forming a more stable complex with platinum (Cl^- [9, 10], Br^- [11], pyridine [12], imidazole [13]) dramatically decreases the reductive elimination rate: no reaction occurs even at $\text{L} = \text{Cl}^-$.



Scheme 3.

Kinetically, this is manifested as the fact that the dependence of the apparent rate constant k on the nucleophile concentration is described by the following equation [9–16]:

$$k = k_{\text{Nu}}[\text{Nu}]/(1 + K_{\text{L}}[\text{L}]), \quad (1)$$

where k_{Nu} is the rate constant of the reaction between R-Pt^{IV} and the nucleophile Nu and K_{L} is the equilibrium constant (see Scheme 3):

$$K_{\text{L}} = [\text{L-Pt}^{\text{IV}}\text{-R}]/([\text{L}][\text{H}_2\text{O-Pt}^{\text{IV}}\text{-R}]). \quad (2)$$

In the general case, Nu and L may be the same (e.g., $\text{Nu} = \text{L} = \text{Cl}^-$ [9–11] and Br^- [12]) or different (e.g., $\text{Nu} = \text{Cl}^-$ and $\text{L} = \text{Py}$ [13] or Im [14]).

Luinstra et al. [8] did not determine the pH of the solution. As judged from their results, measurements were taken at $\text{pH} < 7$. It is likely for this reason that the possibility of intramolecular reductive elimination was not discussed (see below).

Here, we report the decomposition kinetics of platinahydrins **1** and **2** in aqueous buffer solutions at $\text{pH} 7\text{--}8$.

RESULTS AND DISCUSSION

After holding a solution of **1** ($\sim 5 \times 10^{-5} \text{ mol/l}$) in 0.5 M HCl at 25°C for 4 h, absorbance at $\lambda = 262 \text{ nm}$ is unchanged; that is, β -hydroxyethylplatinum(IV) is fairly stable under these conditions, which is in agree-

Table 1. Dependence of the rate constant of the reductive elimination of ethylene oxide from the complex $\text{Cs}_2\text{Pt}(\text{CH}_2\text{CH}_2\text{OH})\text{Cl}_5$ (**1**) on the acidity of the medium

pH	$k \times 10^3, \text{s}^{-1}$
6.63	0.112 ± 0.002
7.03	0.152 ± 0.002
7.23	0.230 ± 0.001
7.40	0.298 ± 0.003
8.20	1.56 ± 0.03
8.20	1.68 ± 0.01
8.45	2.27 ± 0.05
8.58	3.04 ± 0.05
8.72	2.86 ± 0.09
8.80	4.29 ± 0.03
8.97	7.20 ± 0.09

Note: The solvent is water; $T = 298 \text{ K}$; $[\text{NaCl}] = 3.0 \text{ mol/l}$.

Table 2. Dependence of the rate constant of the reductive elimination of ethylene oxide from complex (**1**) on the Cl^- concentration

$[\text{Cl}^-], \text{mol/l}$	$k \times 10^3, \text{s}^{-1}$	
	observed	calculated
0.00	2.56 ± 0.03	2.50
0.07	2.25 ± 0.02	2.19
0.20	1.72 ± 0.02	1.78
0.39	1.64 ± 0.01	1.46
0.91	1.07 ± 1.07	1.01
1.50	0.83 ± 0.01	0.79
2.50	0.63 ± 0.01	0.63
3.00	0.66 ± 0.01	0.58

Note: The solvent is water; $T = 298 \text{ K}$; pH 8.15; $[\text{NaCl} + \text{NaClO}_4] = 3.0 \text{ mol/l}$.

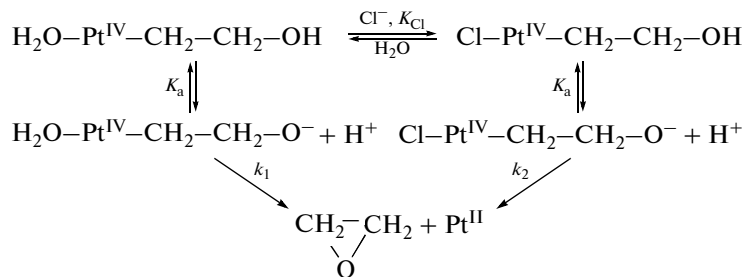
ment with earlier data [8]. The decomposition of **1** yielding gaseous ethylene (identifiable by GLC) is observed only when the complex is heated in concentrated HCl in a boiling water bath.

In salt solutions ($[\text{NaCl}] + [\text{NaClO}_4] = 3.0 \text{ mol/l}$), complexes **1** and **2** decompose at an appreciable rate, but the kinetics of these process does not obey a simple first-order equation: the slope of the $\ln D-t$ curve, where D is absorbance and t is the reaction time, decreases during the run (see, e.g., Fig. 1). The main decomposition products of **2** under these conditions are 1,3-dichloropropan-2-ol and epichlorohydrin, whose yields, as determined by GLC, are 35 and 65%, respectively.

These kinetic deviations are not observed when the reaction is conducted in a buffer solution: at $\text{pH} \geq 7$, **1** and **2** decompose according to a first order equation with respect to platinum(IV). The reaction rate under these conditions is well above the reaction rate in the solutions containing only NaCl and NaClO_4 . For this reason, these experiments were performed at a lower temperature of 298 K. Special-purpose experiments demonstrated that the decrease in the absorbance of the R-Pt^{IV} solution is due only to reductive elimination: the UV spectra of solutions of K_2PtCl_6 and $\text{Cs}_2\text{PtCl}_4(\text{CH}_3)$ (10^{-5} mol/l) containing 3 M NaCl or NaClO_4 at pH 8.15 do not change within the measurement time, suggesting that equatorial chloro ligand are not replaced by hydroxo or aqua ligands. Note that no glycol and chlorohydrin formation from **1** and **2** is observed at $\text{pH} \geq 7$ and the only products detectable by GLC and $^1\text{H NMR}$ [9, 11] are ethylene oxide and epichlorohydrin, respectively.

Tables 1 and 2 list the rate constants of the reductive elimination of ethylene oxide from complex **1** at various pH values and chloride ion concentrations. Unlike the other known reductive eliminations from $\text{R-Pt}(\text{IV})$, this reaction speeds up as the acidity of the medium decreases and is slowed down by Cl^- . Since the primary decomposition product at $\text{pH} > 7$ is ethylene oxide, it is natural to assume that, under the conditions examined, **1** decomposes intramolecularly via a nucleophilic attack of the hydroxyethyl oxygen atom on the carbon atom bonded to platinum. According to this mechanism, the concentration of the nucleophile (see Scheme 1) does not appear in the kinetic equation (1), which takes the following form at $\text{Nu} = \text{L} = \text{Cl}$:

$$k = k_{\text{Cl}} / (1 + K_{\text{Cl}}[\text{Cl}^-]). \quad (3)$$



Scheme 4.

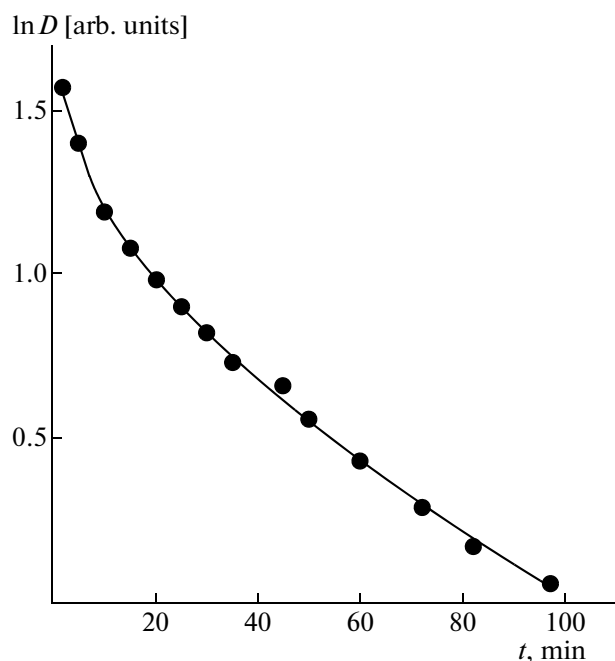


Fig. 1. Semilogarithmic plot of the absorbance of the solution versus time for the decomposition of complex **1** (water as the solvent, $T = 323$ K, $[\text{NaCl}] = 0.125$ mol/l, $[\text{NaClO}_4] = 0.375$ mol/l).

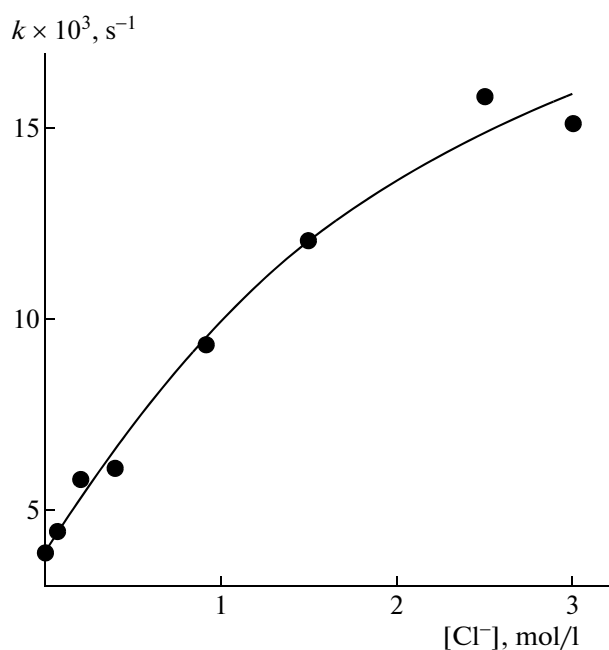


Fig. 2. k^{-1} versus $[\text{Cl}^-]$ for the reductive elimination of ethylene oxide from complex **1** (water as the solvent, $T = 298$ K, pH 8.15, $[\text{NaCl}] = 3.0$ mol/l).

However, the reductive elimination rate constants determined in this study disobey Eq. (3): k^{-1} as a function of $[\text{Cl}^-]$ is nonlinear (Fig. 2). This behavior is consistent with Scheme 4, which includes the intramolecular nucleophilic attack of the alkoxide both in the complex with an aqua ligand *trans* to the alkyl group and in the complex with a chloride ligand in the same position. The following kinetic equation corresponds to this mechanism at $[\text{Pt}^{\text{IV}}-\text{CH}_2-\text{CH}_2-\text{O}^-] \ll [\text{Pt}^{\text{IV}}-\text{CH}_2-\text{CH}_2-\text{OH}]$ (which is typically the case for aqueous solutions of alcohols):¹

$$k = (k_1 + k_2 K_{\text{Cl}} [\text{Cl}^-]) / (1 + K_{\text{Cl}} [\text{Cl}^-]), \quad (4)$$

where k_1 and k_2 are the rate constants of intramolecular reductive elimination via the mechanism presented in Scheme 4. Nonlinear regression calculations give, for pH 8.15, the following values of k_1 , k_2 , and the equilibrium constant K_{Cl} (with a multiple correlation coefficient of $R = 0.990$): $k_1 = 0.0025 \pm 0.0001$ s⁻¹, $k_2 = 0.0003 \pm 0.0001$ s⁻¹, and $K_{\text{Cl}} = 2.3 \pm 0.5$ mol/l.

The goodness of fit between the experimental data and Eq. (4) with the above values of the rate and equilibrium constants is illustrated by the data presented in Table 2, in which the experimental rate constants of the reductive elimination of ethylene oxide from **1** are compared with the corresponding calculated data.

Table 3 lists the decomposition rate constants measured for the complex $\text{Cs}_2\text{PtCl}_5(\text{CH}_2\text{CHOHCH}_2\text{Cl})$ at

¹ Here, the measured rate constant k is an effective quantity: $k = k' K_{\text{a}} [\text{Pt}^{\text{IV}}-\text{CH}_2-\text{CH}_2-\text{OH}] / [\text{H}^+]$.

298 K in buffer solutions with pH 8.15. The reductive elimination rate constant in this case is a more complicated function of $[\text{Cl}^-]$, passing through a maximum (Fig. 3). This dependence can be qualitatively explained in terms of the reaction proceeding according to Scheme 5.

As distinct from ethyleneplatinahydrin, ($\text{Pt}^{\text{IV}}-\text{CH}_2\text{CH}_2\text{OH}$), β -platinumchloropropanol, and ($\text{Pt}^{\text{IV}}-\text{C}^{\alpha}\text{H}_2-\text{C}^{\beta}\text{H}(\text{OH})-\text{C}^{\gamma}\text{H}_2\text{Cl}$) each have two reactive sites accessible to intramolecular attack by the alkoxide oxygen atom. Attack on the α -carbon atom leads to the formation of reductive elimination products, namely, epichlorohydrin and a platinum(II) complex. Attack on the γ -carbon atom yields epiplatinahydrins (**2c** and **2d**) in equilibrium with the initial complex. The presently available experimental data are insufficient to calculate all of the rate and equilibrium constants appearing in Scheme 5. However, if the contribution from inner-sphere reductive elimination from the complex containing a chloride ligand *trans* to the alkyl group is neglected (the inequality $k_2 \ll k_1$ is assumed to be true, as in the case of β -hydroxyethylplatinum), it can be demonstrated that, in the first approximation, the apparent rate constant of $\text{Pt}^{\text{IV}}-\text{CH}_2-\text{CH}(\text{OH})\text{CH}_2\text{Cl}$ decomposition is given by

$$k = k_1 [\text{Cl}^-] / \{K_1 + (1 + K_{\text{Cl}} K_2) [\text{Cl}^-] + K_{\text{Cl}} [\text{Cl}^-]\} \quad (5)$$

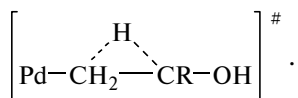
with $k_1 = 0.0034$ s⁻¹, $K_{\text{Cl}} = 2.40$ l/mol, $K_1 = 0.37$ mol/l, and $K_2 = 0.18$ mol/l. It is clear from Fig. 3 that Eq. (5) with the above rate and equilibrium constants

Table 3. Dependence of the rate constant of the reductive elimination of epichlorohydrin from complex **2** on the Cl^- concentration

$[\text{Cl}^-]$, mol/l	$k \times 10^3$, s^{-1}
0.00	0.61 ± 0.01
0.20	0.82 ± 0.01
0.40	1.15 ± 0.01
0.72	1.06 ± 0.03
1.00	0.68 ± 0.01
1.50	0.63 ± 0.02
2.00	0.32 ± 0.01
2.50	0.40 ± 0.01
3.00	0.25 ± 0.01

Note: The solvent is water; $T = 298 \text{ K}$; $\text{pH } 8.15$; $[\text{NaCl} + \text{NaClO}_4] = 3.0 \text{ mol/l}$.

ing intramolecular nucleophilic attack by the hydride ion in the transition state:



When this reaction is conducted in excess oxidizer (CuCl_2), the formation of carbonyl compounds is accompanied by the formation of chlorohydrins [18, 19]. The relevant data available from the literature [20–22] are quite consistent with the mechanisms

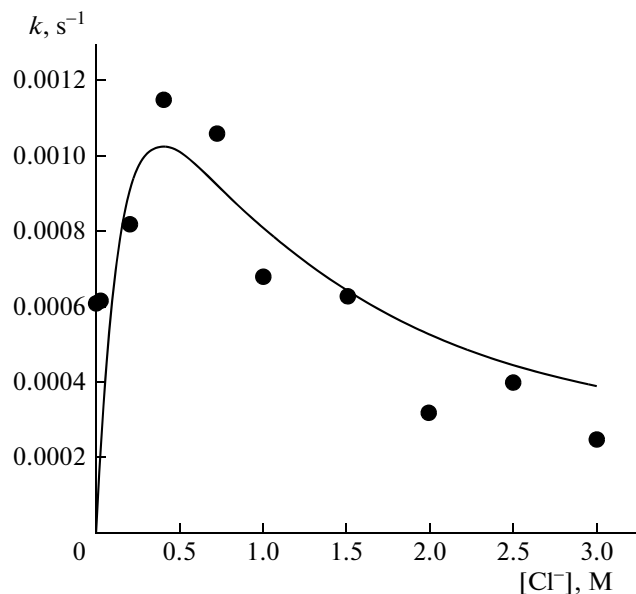


Fig. 3. The rate constant of the reductive elimination of epichlorohydrin from complex **2** as a function of the chloride ion concentration (water as the solvent, $T = 298 \text{ K}$, $\text{pH } 8.15$, $[\text{NaCl}] = 3.0 \text{ mol/l}$). The points represent experimental data, and the line represents the data calculated using Eq. (5).

involving outer-sphere attack by chloride ions on Pd(II) hydrin–oxidizer intermediate complexes or on Pd(IV) hydrins, $\text{Pd}^{\text{IV}}-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_2-\text{R}$.

It is likely that intramolecular reductive elimination yielding olefin oxides will be observed for palladium and mercury derivatives if $\text{M}-\text{RO}^-$ species are generated under conditions such that the leaving group Pd^0 or Hg^0 is additionally stabilized, e.g., by conducting the reaction in the presence of palladium black or mercury metal.

EXPERIMENTAL

The decomposition kinetics of platinum(IV) complexes was studied spectrophotometrically (SF-16 spectrophotometer) by monitoring the decreasing absorbance of their solution at a wavelength of $\lambda = 262 \text{ nm}$, which corresponds absorption maximum for the platinum(IV) complexes [12]. When the platinum complex concentration is far below the concentration of the Cl^- ligand and when the equilibrium between different platinum(IV) species is established rapidly, absorbance at the given wavelength is directly proportional to the total concentration of the platinum(IV) complexes. Decomposition rate constants were derived from the slopes of $\ln(D - D_\infty) - t$ straight lines.

Ethyleneplatinahydrin complexes **1** and **2** were synthesized via earlier reported procedures (see [9] and [5], respectively) by reacting the corresponding α -oxide with K_2PtCl_4 solutions in aqueous HClO_4 . The products were isolated as comparatively low-soluble cesium derivatives, $\text{Cs}_2\text{Pt}(\text{R})\text{Cl}_5$, by adding a saturated CsCl solution to the redaction mixture.

Buffer solutions were prepared by dissolving Na_3PO_4 and H_3PO_4 in bidistilled water. The chloride ion concentration was varied using NaClO_4 (reagent grade). Ionic strength was maintained with NaClO_4 (reagent grade). The pH of the resulting solutions was measured with an I-02 pH meter.

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REFERENCES

- Collman, J.P., Hegedus, L.S., Norton, J.R., and Finke, R.G., *Principles of Organotransition Metal Chemistry*, Mill Valley, Calif.: Univ. Science Books, 1987, vol. 1.
- Moiseev, I.I., *π -Kompleksy v zhidkofaznom okislenii olefinov* (π -Complexes in Liquid-Phase Alkene Oxidation), Moscow: Nauka, 1970.
- Handbook of Organopalladium Chemistry for Organic Synthesis*, Negishi, E., Ed., New York: Wiley, 2002.

4. Makarova, L.G. and Nesmeyanov, F.N., *Metody elementoorganicheskoi khimii. Rtut'* (Methods of Organoelement Chemistry: Mercury), Moscow: Nauka, 1965.
5. Chanysheva, I.R., Litvinenko, S.L., and Vdovichenko, A.N., *Izv. Akad. Nauk, Ser. Khim.*, 2002, no. 2, p. 332.
6. Halpern, J. and Tewsburg, R.A., *J. Organomet. Chem.*, 1979, vol. 181, p. 223.
7. Khusnutdinova, J.R., Zavalij, P.Y., and Vedernikov, A.N., *Organometallics*, 2007, vol. 26, p. 2402.
8. Luinstra, G.A., Wang, L., Stahl, S.S., Labinger, J.A., and Bercaw, J.E., *J. Organomet. Chem.*, 1995, vol. 504, p. 75.
9. Zamashchikov, V.V., Litvinenko, S.L., and Shologon, V.I., *Kinet. Katal.*, 1987, vol. 28, p. 1059.
10. Mitchenko, S.A., Zamashchikov, V.V., Pryadko, O.N., and Vdovichenko, A.N., *Metalloorg. Khim.*, 1989, vol. 2, p. 741.
11. Zamashchikov, V.V., Litvinenko, S.L., and Popov, V.G., *Metalloorg. Khim.*, 1991, vol. 4, p. 709.
12. Litvinenko, S.L., Zamashchikov, V.V., Garkusha-Bozhko, V.S., and Uzhik, O.N., *Ukr. Khim. Zh.*, 1986, vol. 52, p. 1281.
13. Litvinenko, S.L., Zamashchikov, V.V., and Shologon, V.I., in *Tez. dokl. IV Vses. konf. po metalloorganicheskoi khimii* (Proc. IV All-Union Conf. on Organometallic Chemistry), Kazan, 1988, III-21.
14. Mitchenko, S.A. and Zamashchikov, V.V., *Kinet. Katal.*, 1989, vol. 30, p. 297.
15. Litvinenko, S.L., Shologon, V.I., Zamashchikov, V.V., and Bilobrov, S.V., *Metalloorg. Khim.*, 1991, vol. 4, p. 1130.
16. Litvinenko, S.L., Shologon, V.I., and Zamashchikov, V.V., *Metalloorg. Khim.*, 1991, vol. 4, p. 471.
17. Zamashchikov, V.V., Mitchenko, S.A., and Slinkin, S.M., *Izv. Akad. Nauk, Ser. Khim.*, 1994, no. 3, p. 518.
18. Stang, L.H. and Jira, R., *Tetrahedron Lett.*, 1970, vol. 11, p. 3589.
19. Hamed, O., Thompson, C., and Henry, P.M., *J. Org. Chem.*, 1997, vol. 62, p. 7082.
20. Backvall, J.-E., Akermark, B., and Ljunggren, S.O., *J. Am. Chem. Soc.*, 1979, vol. 101, p. 2411.
21. Pshenichnikova, A.B., Brailovskii, S.M., and Temkin, O.N., *Kinet. Katal.*, 1989, vol. 30, p. 92.
22. El-Qisairi, A., Hamed, O., and Henry, P.M., *J. Org. Chem.*, 1998, vol. 63, p. 2790.