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COORDINATION COMPOUNDS

Kinetics of Reactions between Bromoplatinum(II) Complexes and Silver Nitrate

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Abstract—The kinetics of the reactions of bromide complexes [[$PtenBr_2$], [$Pt(NH_3)_2Br_2$], and [$enPtBr_2Pten$]$(NO_3)_2$ with $AgNO_3$ are studied potentiometrically. The reactions occur in two stages with dramatically different rates. Rate constants are determined for the second stage. The kinetics of the reaction between the dimeric complex and $AgNO_3$ are studied at 5, 15, 25, and 35°C. The activation energy is determined.

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In reactions between stoichiometric amounts of haloplatinum(II) complexes and silver nitrate, halide ions even at ambient temperature are almost completely eliminated from the inner sphere of the complexes and precipitated as silver halide, e.g.,

$$[Pt(NH_3)_2Br_2] + 2AgNO_3 + 2H_2O = [Pt(NH_3)_2(H_2O)](NO_3)_2 + 2AgBr\downarrow.$$

This work concerns the kinetics of the reaction between silver nitrate and platinum(II) complexes, either monomeric ([$PtenBr_2$] or [$Pt(NH_3)_2Br_2$]) or dimeric ([$enPtBr_2Pten$]$(NO_3)_2$, where en stands for ethylenediamine and *m* for methylamine), the latter containing two bridging bromine atoms.

EXPERIMENTAL

[$PtenCl_2$] and *trans*-[$Pt(NH_3)_2Cl_2$] were synthesized according to [1].

The synthesis of the dimeric complex [$enPtBr_2Pten$]$(NO_3)_2$ is described in [2].

The Ag^+ concentrations in solutions were determined on an ANION-410 pH meter/conductometer using a silver ion-selective electrode and an Ag/AgCl saturated reference electrode. A calibration curve was plotted as the emf versus Ag^+ concentration in standard solutions ($c = 1 \times 10^{-2}, 1 \times 10^{-3}, 1 \times 10^{-4}, 1 \times 10^{-5}$ mol/L).

The temperature of test solutions was adjusted accurate to ±0.5°C with a thermostat.

Kinetic experiments were carried out at the starting concentration of the complex equal to 1×10^{-3} mol/L. The solutions were prepared by inserting the calculated amount of the complex to a 0.3 M sodium nitrate solution. Silver nitrate was added as an aqueous solution with $c = 0.025$ mol/L.

RESULTS AND DISCUSSION

Kinetic experiments consisted of measurements over time of the emf of galvanic cells built of a silver ion-selective indicator electrode and an Ag/AgCl reference electrode.

The substitution of a water molecule for each inner-sphere bromide ion Br^- adds unity to the charge of the complex. It was natural to suggest that the reaction of a complex containing two bromide ions with silver nitrate would occur in two stages at substantially differing rates:

$$(1)\ [PtenBr_2] + Ag^+ + H_2O = [PtenBrH_2O]^+ + AgBr\downarrow,$$

$$(2)\ [PtenBrH_2O]^+ + Ag^+ + H_2O = [Pten(H_2O)_2]^{2+} + AgBr\downarrow;$$

and

$$(1)\ [Pt(NH_3)_2Br_2] + Ag^+ + H_2O = [Pt(NH_3)_2BrH_2O]^+ + AgBr\downarrow,$$

$$(2)\ [Pt(NH_3)_2BrH_2O]^+ + Ag^+ + H_2O = [Pt(NH_3)_2(H_2O)_2]^{2+} + AgBr\downarrow.$$

Table 1. Kinetics of the reaction between $[PtenBrH_2O]NO_3$ and silver nitrate at 25°C

Time, s	c_{AgNO_3}, mol/L	k
0	0.0010	
10	0.00089	11.48
20	0.00080	12.50
30	0.00073	12.20
40	0.00068	11.34
50	0.00062	11.85
60	0.00058	11.63
70	0.00054	11.93
80	0.00050	12.20
90	0.00048	11.85
100	0.00046	11.37
110	0.00044	11.29
120	0.00041	11.84
130	0.00039	11.98
140	0.00038	11.65
150	0.00036	11.70
160	0.00034	11.76
170	0.00033	11.62
190	0.00031	11.50
200	0.00029	11.83
210	0.00029	11.55
230	0.00027	11.46
240	0.00027	10.98
250	0.00026	11.15
260	0.00025	11.00
270	0.00025	10.94
280	0.00024	11.31
		11.66 ± 0.36

At the first stage of the reaction of silver nitrate with the dimeric complex, one bromide bridge should be broken, and at the second, a monomeric aqua complex should form:

$$(1)\ [enPtBr_2Pten]^{2+} + Ag^+ + 2H_2O = [en(H_2O)PtBrPt(H_2O)en]^{3+} + AgBr\downarrow,$$

$$(2)\ [en(H_2O)PtBrPt(H_2O)en]^{3+} + Ag^+ + 2H_2O = 2[Pten(H_2O)_2]^{2+} + AgBr\downarrow.$$

The kinetics of the first reaction stage were studied as follows: an ion-selective electrode was immersed into the aqueous solution of the complex with $NaNO_3$ background, silver nitrate was added in a proportion of 1 mol per mole of the complex, and the emf of the galvanic cell was measured over time. The silver concentration in the solutions decreased so quickly that it was impossible to determine rate constants: reactions with *cis*-diamine and the dimer came virtually to the end in 70–100 s and those with *trans*-diamine in 20 s in agreement with the trans-influence laws.

After the first stage ended, a new silver nitrate increment was added to the solution in a proportion of 1 mol per mole of the complex, and measurements were continued. The silver-ion concentrations were used to calculate the rate constant of the second reaction stage using the rate equation for a second-order reaction,

$$k = \frac{c_0 - c}{\tau c_0 c},$$

where c_0 is the starting silver(I) ion concentration and c is the silver(I) ion concentration τ seconds after the reaction onset.

The rate constants calculated from the above equation remained virtually the same during the experiment.

Tables 1–3 display the experimental data and rate constants for the test complexes at 25°C.

Comparison between the rate constants listed in Tables 1 and 2 shows that the rate of the reaction of silver nitrate with $[PtenBrH_2O]NO_3$ is almost two times that with *trans*-$[Pt(NH_3)_2BrH_2O]NO_3$. This seems natural in view of the fact that the coordinated bromide ion in the monomeric complex is trans to the amine molecule, which has a stronger trans-influence than a water molecule [3].

Table 3 shows that the bridging bromide ion reacts with the silver(I) ion more rapidly than the terminal bromide ions. We observed this effect previously in studies of the reaction kinetics of bromide complexes with potassium iodide.

To estimate the activation energy for the reaction of the dimeric complex $[en(H_2O)PtBrPt(H_2O)en](NO_3)$

Table 2. Kinetics of the reaction between *trans*-$[Pt(NH_3)_2BrH_2O]NO_3$ and silver nitrate at 25°C

Time, s	c_{AgNO_3}, mol/L	k
0	0.00050	
195	0.00030	6.84
210	0.00029	6.90
240	0.00028	6.55
265	0.00027	6.436
285	0.00026	6.488
305	0.00025	6.56
330	0.00024	6.57
365	0.00023	6.43
400	0.00022	6.36
440	0.00021	6.28
480	0.00020	6.25
505	0.00019	6.46
580	0.00018	6.13
645	0.00017	6.02
		6.45 ± 0.23

Table 3. Kinetics of the reaction between $[en(H_2O)PtBrPt(H_2O)en](NO_3)_3$ and silver nitrate at 25°C

Time, s	c_{AgNO_3}, mol/L	k
0	0.0010	
70	0.00028	36.73
80	0.00026	34.67
90	0.00024	35.18
100	0.00022	35.45
110	0.00020	35.04
120	0.00019	35.53
130	0.00017	36.52
140	0.00016	37.50
160	0.00014	35.98
190	0.00013	35.54
220	0.00012	34.64
235	0.00011	34.43
245	0.00010	36.73
260	0.000098	35.40
270	0.000097	34.48
280	0.000090	36.11
285	0.000089	35.92
300	0.000084	36.35
315	0.000083	35.07
325	0.000082	34.45
330	0.000081	34.15
340	0.000080	33.60
345	0.000080	33.33
350	0.000080	32.86
		35.23 ± 1.12

with silver nitrate, we studied the kinetics of this reaction at 5, 15, and 35°C (Tables 4–6).

The figure demonstrates the $\ln k = f(1/T)$ plot for this reaction. The activation energy found from this plot is 83.1 kJ/mol. Thus, the reaction of the dimeric com-

Table 4. Kinetics of the reaction between $[en(H_2O)PtBrPt(H_2O)en](NO_3)_3$ and silver nitrate at 5°C

Time, s	c_{AgNO_3}, mol/L	k
0	0.001	
162	0.00055	4.92
180	0.00053	4.85
200	0.00053	4.43
210	0.00052	4.36
220	0.00051	4.37
230	0.0005	4.35
250	0.00048	4.33
260	0.00047	4.34
280	0.00045	4.37
290	0.00044	4.39
310	0.00042	4.45
320	0.00041	4.50
340	0.00039	4.60
360	0.00038	4.53
370	0.00037	4.60
390	0.00036	4.56
410	0.000347	4.59
430	0.000336	4.60
450	0.000336	4.39
472	0.00032	4.50
480	0.00032	4.43
500	0.000314	4.37
525	0.000303	4.38
570	0.000297	4.15
		4.48 ± 0.16

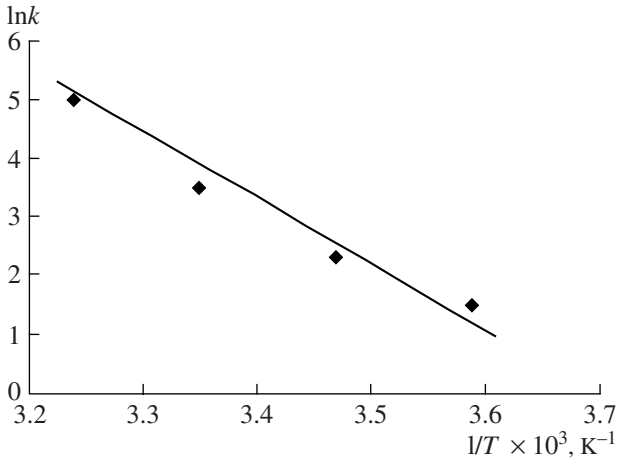
Table 5. Kinetics of the reaction between $[en(H_2O)PtBrPt(H_2O)en](NO_3)_3$ and silver nitrate at 15°C

Time, s	c_{AgNO_3}, mol/L	k
0	0.001	
70	0.00057	10.69
100	0.00048	10.83
120	0.00044	10.60
130	0.00043	10.20
140	0.00041	10.28
150	0.00039	10.43
160	0.00038	10.20
170	0.00038	9.60
180	0.00036	9.88
190	0.00035	9.78
210	0.00033	9.67
220	0.00032	9.66
240	0.0003	9.72
260	0.00028	9.90
280	0.00026	10.16
300	0.00024	10.56
350	0.00021	10.37
370	0.00020	10.55
400	0.00019	10.52
470	0.00018	9.31
520	0.00016	10.10
552	0.00015	9.80
600	0.00014	9.91
642	0.00013	9.73
		10.10 ± 0.39

Table 6. Kinetics of the reaction between $[en(H_2O)PtBrPt(H_2O)en](NO_3)_3$ and silver nitrate at 35°C

Time, s	c_{AgNO_3}, mol/L	k
0	0.001000	–
30	0.000180	151.85
50	0.000120	152.41
70	0.000086	151.83
85	0.000072	151.63
90	0.000069	149.92
100	0.000063	148.73
110	0.000058	147.65
120	0.000053	148.90
130	0.000049	149.30
140	0.000046	148.14
150	0.000043	148.37
160	0.000040	150.00
170	0.000038	148.91
180	0.000036	148.77
190	0.000034	149.54
200	0.000032	151.25
210	0.000031	148.85
220	0.000029	152.19
250	0.000026	149.85
280	0.000023	151.70
		150.00 ± 1.52

plex with silver nitrate has a higher rate and a lower activation energy than the reaction of the same complex with potassium iodide [4].



Plot ln$k$ vs. $1/T$ for the reaction of $[en(H_2O)PtBrPt(H_2O)en](NO_3)_3$ with silver nitrate.

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