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The Kinetics of the Reaction of Bipyridyl with Potassium Trichloro (2,5-dimethyl 3-hexyne 2,5-diol)Platinate(II)

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The substitution reaction of bipyridyl with potassium trichloro (2,5-dimethyl 3-hexyne 2,5-diol) platinate(II) has been studied in 90% methanol –10 water mixtures at various temperatures. The reaction proceeds in several steps of which two have been well defined. Two rate constants were measured at 25°C:

$$k_{1obs.} = 25\times 10^{-3}\ sec^{-1}$$
$$k_{2obs.} = 0.2\times 10^{-3}\ sec^{-1}$$

The first constant depends on the bipyridyl concentration and the second is independant of bipyridyl concentration. The rate constants found compared with those of Zeise's salt suggest a greater trans *effect for the acetylenic glycol, as compared to the ethylene.*

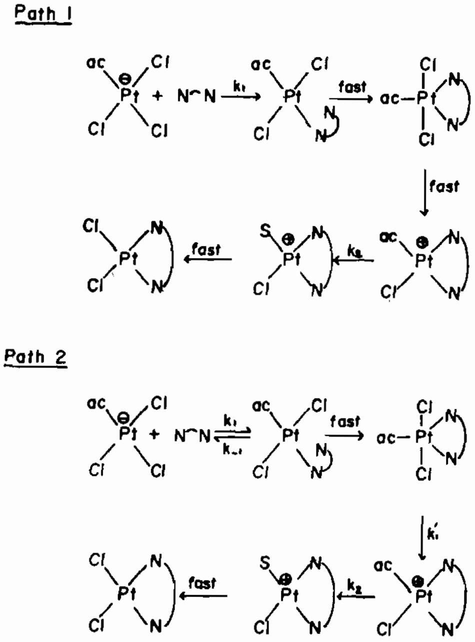
Introduction

Kinetic studies of the d^8 systems is an important and rapidly expanding research field in homogeneous catalysis. Substitution reactions of platinum(II) complexes have been extensively studied.[1] However, there are few data concerning the kinetics of substitution of d^8 systems, and in particular the platinum(II) complexes with bidentate ligands. The kinetic study of Zeise's salt, $K[PtC_2H_4Cl_3]$, with 2,2'-bipyridyl(bip) has been recently reported by Uguagliati *et al.*[2]

In the present work we have studied the analogous Bukhovets' salt, $K[Pt(ac)Cl_3]$, where ac = 2,5-dimethyl 3-hexyne 2,5-diol, $(CH_3)_2C(OH)C\equiv CC(OH)(CH_3)_2$ in order to get more data on these systems and obtain information on the mechanism of the following reaction:

$$[Pt(ac)Cl_3]^- + bip \longrightarrow cis\text{–}[Pt(bip)Cl_2] + ac + Cl^-$$

Uguagliati *et al* [2] have proposed a mechanism for the reaction of Zeise's salt with the same ligand involving a bimolecular attack of the bipyridyl to give a cationic complex as an intermediate, which loses the olefin to give the more stable *cis*–$[Pt(bip)Cl_2]$ complex. This mechanism is similar to that in path 1 (Scheme I). The authors in that paper presented some kinetic evidence for the presence of the cationic complex $[PtC_2H_4Clbip]Cl$.



Scheme I

We have recently reported a series of well characterized cationic complexes of the general formula $[Pt(ac)(en)Cl]Cl$, where en = ethylenediamine and ac = an acetylenic derivative.[4]

Prompted by the study of Uguagliati et *al*[2] on Zeise's salt, we have undertaken the investigation of the displacement of the chlorines in $[Pt(ac)Cl_3]^-$ ion with bipyridyl. The two series of complexes, *i.e.*, platinum(II) olefin and acetylene complexes are very similar in their solution reactions.[3] The *trans* chlorine is strongly labilized.

We also wish to report here the isolation of the cationic complex $[Pt(ac)Cl(bip)]Cl$, the rate of formation of this from $[Pt(ac)Cl_3]^-$ and the rate of replacement of the acetylenic ligand.

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(1) F. Basolo and R. G. Pearson, « Mechanisms of Inorganic reactions », John Wiley and Sons, Inc., New York, 1968; and C. H. Langford and H. B. Gray, « Ligand Substitution processes », W. A. Benjamin Co., New York, N. Y. 1965.
(2) P. Uguagliati, U. Belluco, U. Croatto, and P. P. Rosario, *J. Am. Chem. Soc.*, *89*, 1336, (1967).
(3) A. D. Allen and T. Theophanides, *Can. J. Chem.*, *43*, 290 (1965).
(4) P. C. Kong and T. Theophanides, *Can J. Chem.*, *45*, 3193 (1967).

Experimental Section

Materials. The complex K[Pt(ac)Cl$_3$] used in the reactions was prepared according to the method of Bukhovets modified by Allen and Theophanides.[3] The product was then recrystallized from a mixture of acetone and ether.

The complex [Pt(ac)(bip)Cl]Cl was prepared by the method of Kong and Theophanides.[4] The melting point, infrared and ultra-violet spectra of the end-product *cis*–[Pt(bip)Cl$_2$] are similar to the *cis*–[Pt(bop)Cl$_2$] complex, prepared according to Morgan and Burstal.[5] The analysis of [Pt(ac)(bip)Cl]Cl gives for C, 38.56%; H, 4.07; Pt, 34.91% compared with calculated C, 38.31%; H, 3.93%; Pt, 34.57%.

The methanol was purified by distilling over Mg(OCH$_3$)$_2$ and the other materials were reagent grade products. The ligand bipyridyl was also recrystallized before use.

Kinetics runs: The reactions were studied by measuring the optical density changes in the spectral region 3300-4000 Å. Survey spectra were recorded, as a function of time with a « Bausch and Lomb-Spectronic 505 »-spectrophotometer. Freshly prepared solutions of K[Pt(ac)Cl$_3$] were used each time known volumes of thermostated solutions of the complex and the reagents were mixed in a 1 cm path quartz cell.

The rate constants were calculated from the plot of Log(D$_\infty$–D$_t$) *vs.* time, where D$_t$ is the optical density at time t and D$_\infty$ at an infinite time. The optical density changes were recorded with a Cary 14 spectrophotometer equipped with a thermostated cell compartment.

The ionic strength in all the experiments was kept constant at 0.2 *M* with lithium perchlorate.

Results and Discussion

The various kinetic runs were performed in 90% aqueous methanol (90% methanol - 10% water by volume) solutions at 5, 25, 40 and 50°C. To these solutions hydrochloric acid was added in order to prevent complete aquation of the Bukhovets' salt and to be able to change at will the concentration of the free bipyridyl in solution. Protonation of the bipyridyl reduces its coordination ability and no substitution takes place. The concentrations of the free ligand were calculated from pK$_a$ values given by Harkins[6] in water. The pK$_a$ values in water seem to represent reasonably well the pK$_a$ values in the system methanol-water.[2] The above approximation may affect slightly the value of the bimolecular constant, k$_1$ (see Scheme I), but it does not alter the mechanistic pathway, however. The K$_a$ values at 5 and 50°C were obtained by extrapolation and are given in Table I.

Table I. Acid dissociation constants for 2,2'-bipyridyl[6]

Temperature	$K_a \times 10^5$	$K_a \times 10^5$ (calc.)
5°C	—	3.67
25°C	4.68	—
40°C	5.50	—
50°C	—	6.08

Bukhovets' salt undergoes hydrolysis of the chloride *trans* to the acetylenic ligand in water solutions even in presence of tenfold excess of chloride ion.[3] The hydrolysis constant was found to be 2×10^{-3} *M* at 25°C[3] in water, however in 90% aqueous methanol the hydrolysis becomes less significant and since our runs were done with an excess of chloride ion (at least 50 fold excess) the presence of the *trans* aquo-complex does not seem to modify our conclusions on the kinetics of substitution in the first step of the replacement of the chlorine *trans* to the acetylene.

The rate constants were measured in the presence of an excess of the ligand bipyridyl under pseudo-first order conditions. The changes of the electronic spectra of the reaction mixtures between 3300 and 4000 Å, show that there are at least two steps in the reaction.

The first step is shown with the increase of the optical density as a function of time in all regions of the spectra (see Figure 1).

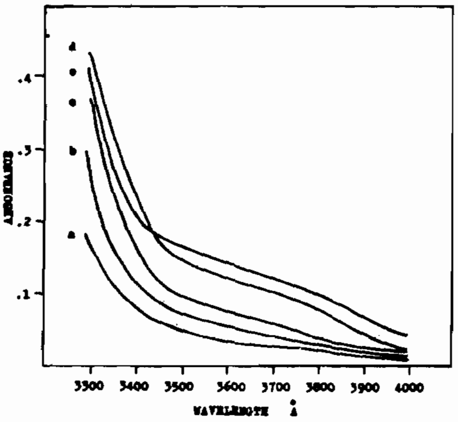

Figure 1. Absorbance changes for the reaction of K[Pt(ac)Cl$_3$] (10^{-4} *M*) with bipyridyl (10^{-3} *M*) in aqueous methanol solutions acidified with HCl (0.1 N) at 25°C. a) Spectrum after ~30 sec.; b) ~3 min.; c) ~4 min.; d) ~9 min.; e) ~10 min.

The second step is shown by the presence of an isobestic point at 3450 Å (see Figure 2). The time of appeareance of the isobestic point is a function of the concentration of hydrochloric acid. From these observations we were able to calculate two experimental rate constants.

The first constant k$_{1obs.}$ was measured at the isobestic point and the second constant k$_{2obs.}$ was measured at a wavelength where the difference in optical density between the spectra of the initial and final products was the largest. These values are shown in Tables II, III, and IV.

The cationic complex [Pt(ac)(bip)Cl]Cl is a white substance and undergoes a slow transformation in the solid state to a yellow product, which we have

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[5] G. T. Morgan and F. H. Burstal, *J. Chem. Soc.*, 965 (1934).
[6] T. R. Harkins, *J .Am. Chem. Soc.*, *77*, 1374 (1955)

found to be a mixture of *cis*–[Pt(bip)Cl$_2$] and ac. In aqueous methanolic solutions the cationic complex gives the same end products, *i.e.*, *cis*–[Pt(bip)Cl$_2$] and ac.

Table II. Rates of reaction in aqueous methanol solutions at 25°C

HCl conc., M	0.2	0.1	0.08	0.05	0.014	0.01	0.005
$k_{1obs.} \times 10^3$ (sec^{-1})	—	6	7	8	18	25	—
$k_{2obs.} \times 10^4$ (sec^{-1})	2.2	2.3	2.1	—	—	2	2.1

Complex conc.: $10^{-4} M$ Total conc. of bipyridyl: $10^{-3} M$

Table III. Rates of reaction in aqueous methanol solutions at 25°C

Complex conc. × $10^4 M$	2	1	0.5
$k_{1obs.} \times 10^3$ (sec^{-1})	5.9	6	6
$k_{2obs.} \times 10^4$ (sec^{-1})	2.1	2.3	2.1

Totale conc. of bipyridyl: $10^{-3} M$ HCl conc.: 0.1 M

Table IV. Rates of reaction at various temperatures:

a) $k_{1obs.}$

Temperature (°C)	5	25	40	50
$k_{1obs.} \times 10^3$ (sec^{-1})	2.5	6	13	16

Total conc. of bip: $10^{-3} M$ HCl conc.: 0.1 M

b) $k_{2obs.} \times 10^4$ (sec^{-1})

Temperature (°C)	5	25	40	50
Conc. HCl, M				
0.1	.39	2.3	9.2	22
0.01	—	2.0	9.3	22
0.005	—	2.1	8.8	20

Total conc. of bip.: $10^{-3} M$ Complex conc.: $10^{-4} M$

Table V. Rate constant, $k_2'_{obs.}$, for the cationic complex, [Pt(ac)(bip)Cl]Cl

Total conc. bip., M	0	10^{-3}
$k_2'_{obs.} \times 10^4$ (sec^{-1})	2.1	2.3

HCl conc.: 0.1 M Complex conc.: $10^{-4} M$ Temperature: 25°C

Kinetic measurements performed with the cationic complex (Figure 3), as a starting material enabled us to determine an isobestic point at 3450 Å under the same conditions as for the kinetic study of the [Pt(ac)Cl$_3$]$^-$ reaction. The rate constant $k_{2obs.}'$ calculated from these data does not depend on the concentration of bipyridyl and its value agrees with the constant $k_{2obs.}$ (Table V). This constant is attributed to the rate of transformation of [Pt(ac)(bip)Cl] into *cis*–[Pt(bip)(Cl$_2$].

Thus the mechanistic process of substitution here may be similar to that proposed by Uguagliati *et al.*[2] and this is shown by path 1 on Scheme I, where the reaction of substitution of the *trans* chlorine takes place by replacing it directly with one end of bipyridyl or *via* the aquo-complex by replacing the *trans* water molecule with the one end of bipyridyl and then a rapid chelation gives the cationic intermediate. The acetylenic ligand in this intermediate is then replaced by one molecule of solvent followed by a quick substitution of the solvent with chloride to give the neutral complex *cis*–[Pt(bip)Cl$_2$].

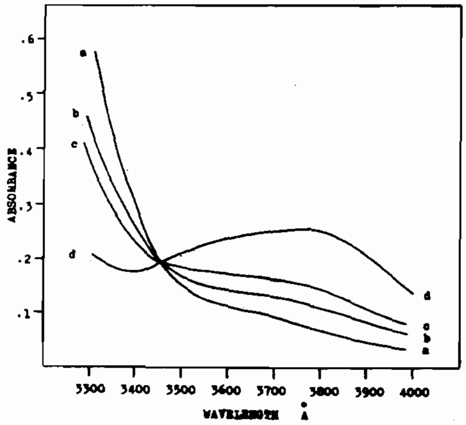

Figure 2. Absorbance changes for the reaction of K[Pt(ac)Cl$_3$] ($10^{-4} M$) with bipyridyl ($10^{-3} M$) in aqueous methanol solutions acidified with HCl (0.1 N) at 25°C. a) Spectrum after 10 min.; b) 15 min.; c) 30 min.; d) final spectrum.

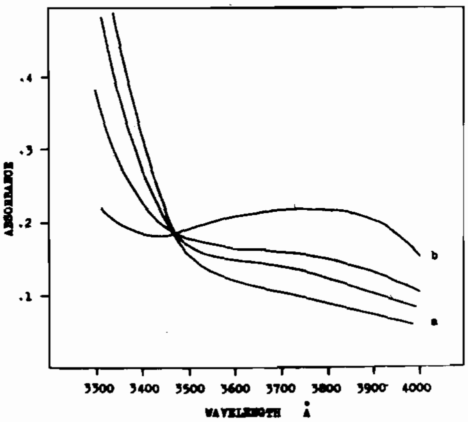

Figure 3. Absorbance changes for the reaction of [Pt(ac)(bip)Cl]Cl ($10^{-4} M$) with bipyridyl ($10^{-3} M$) in aqueous methanol solutions acidified with HCl (0.1 N) at 25°C. a) Spectrum after ~30 sec. b) Final spectrum.

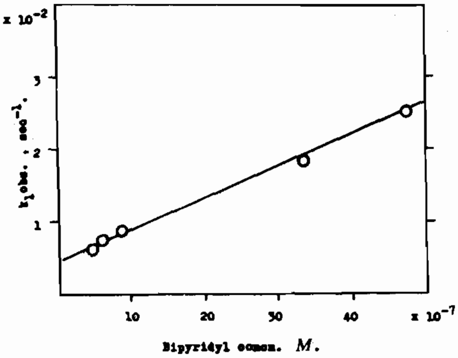

Figure 4. Plot of $k_{1obs.}$ of the reaction of K[Pt(ac)(Cl$_3$] with bipyridyl vs the concentration of free bipyridyl at (Path 1).

Table VI. Variation of k_1 ($sec^{-1}.M^{-1}$) with temperature calculated from the rate law of path 1.

Temperature (°K)	Conc. free bip.	$k_1 \times 10^{-3}$ ($sec^{-1}.M^{-1}$)
278	3.67×10^{-7}	6.8
298	4.68×10^{-7}	12.8
313	5.5×10^{-7}	23.6
323	6.08×10^{-7}	26.3

Table VII. Activation parameters

First step	ΔH^*kcal/mole+6	ΔS^* −20eu/mole
Second step	ΔH^*kcal/mole+18	ΔS^* −15eu/mole

Table VIII. Rate constants for Zeise's salt at 25°C[2]

Conc. HCl, *M*	$k_{1obs.} \times 10^4$ (sec^{-1})	$k_{2obs.} \times 10^3$ (sec^{-1})
0.127	4	—
0.01	67	5
0.004	170	4.8

The rate law in this case is given by equations 1 and 2:

$$k_{1obs.} = k_s + k_1[bip] \qquad (1)$$

$$k_{2obs.} = k_2 \qquad (2)\ \text{(see Figure 4)}$$

The variations of $k_{1obs.}$ with temperature are shown in Table VI and activation parameters in Table VII.

The above mechanism however cannot be accepted in all the cases. It holds, if the chelation and the rearrangement of the intermediate [Pt(ac)(bip)Cl_2] into the cationic complex [Pt(ac)(bip)Cl]Cl is rapid. Our experimental data fit better the proposed mechanistic path 2 (Scheme I), in which the five coordinated species, [Pt(ac)(bip)Cl_2] is another stable intermediate, which rearranges into the cationic complex with a slow rate, the rearrangement being the rate determining step. It is known that in square planar metal complexes substitution is done through an S_N2 mechanism involving a trigonal bipyramid.[1]

We were able to isolate the above intermediate product, whose characteristics agree with the formula of the five coordinate complex [Pt(ac)(bip)Cl_2].[7]

Presently, we are still pursuing our investigations and measurements on the structure and rearrangement of this intermediate compound. However, preliminary results can be explained more satisfactorily with path 2 (Scheme I), in which the rate law is given by equations 3, 4.

$$k_{1obs.} = \frac{k_1 \times k'_1[bip]}{k_{-1}[Cl^-]+k'_1} \qquad (3)$$

$$k_{2obs.} = k_2$$

It is interesting to note that our values of $k_{1obs.}$ and $k_{2obs.}$ obtained for the K[Pt(ac)Cl_3] complex according to the mechanistic path 1 are in line with those obtained by Uguagliati *et al.*[2] (See Table VIII).

Two observations can be made, however, by looking at these results, as compared with those of Uguagliati *et al.*[2]

1) The value of $k_{1obs.}$ for Zeise's salt (6.7×10^{-3} sec^{-1}) is smaller than ours for Bukhovets' salt (25×10^{-3} sec^{-1}) at the same pH(HCl = .01 N).

2) The value of $k_{2obs.}$ for Zeise's salt (5×10^{-3} sec^{-1}) is greater than ours (0.2×10^{-3} sec^{-1}) in the same conditions.

The above differences in rate constants for the two types of complexes reflect the ability of *trans* labilizing effect of the ethylene molecule, as compared to the acetylenic glycol. It is known that the *trans*-effect of the olefins and acetylenes is of the same order.[8] Our kinetic results, however, compared with those of Zeise's salt[2] lead us to propose a greater *trans*-effect for the acetylenic ligand. This is what one would expect for this order, *i.e.*, a greater $k_{1obs.}$ for the acetylenic series, thus a faster substitution of the chlorine. A smaller $k_{2obs.}$ for the acetylenic series, representing the elimnation of the acetylenic ligand in the second step, indicates a slower process than for the elimination of the ethylene molecule. However, the above reasoning can be made only for the mechanistic path 1. In path 2, $k_{1obs.}$ incorporates two constants and this simple picture of *trans* substitution is blurred. Presently we are trying to separate the k_1' and k_1 constants in the 2,2-bipyridyl complex and in a similar series of ethylenediamine complexes.[7]

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(7) J. Hubert and T. Theophanides, to be presented at the 52nd CIC Conference, May 25-28, 1969, Montreal, Quebec.

(8) T. P. Cheeseman, A. L. Odell, *Chem. Comm.*, 1496 (1968).