

## Decomposition of $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(\text{bipyridyl})]$ to $[\text{PtCl}_2(\text{bipyridyl})]$ and Ethylene in Different Solvents

G. NATILE, L. MARESCA, L. CATTALINI

*Istituto di Chimica Generale ed Inorganica, University of Venice, Italy*

U. BELLUCO, P. UGUAGLIATI

*Centro di Chimica Metallorganica del C.N.R., c/o Istituto di Chimica Industriale, University of Padua, Italy*

and U. CROATTO

*Istituto di Chimica Generale ed Inorganica, University of Padua, Italy*

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*The decomposition of the 5-coordinate complex  $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(\text{bipy})]$  to the 4-coordinate  $[\text{PtCl}_2(\text{bipy})]$  and ethylene has been studied in 1,2-dichloroethane and in aqueous methanol (95% v/v). The reaction proceeds with different mechanisms in the two solvents. In 1,2-dichloroethane the 5-coordinate substrate decomposes in a single step with  $\Delta H^\ddagger = 18.6 \pm 0.6 \text{ Kcal mol}^{-1}$  and  $\Delta S^\ddagger = -8 \pm 2 \text{ cal K}^{-1} \text{ mol}^{-1}$ . In aqueous methanol  $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(\text{bipy})]$  gives the cationic ethylene complex  $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}(\text{bipy})]^+$  which then reacts with chloride ion in a slow bimolecular process to form  $[\text{PtCl}_2(\text{bipy})]$  and ethylene.*

### Introduction

The reaction of Zeise's and Bukhovets' salts,  $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]^-$  and  $[\text{Pt}\{(\text{CH}_3)_2(\text{OH})\text{CC}\equiv\text{CC}(\text{OH})-(\text{CH}_3)_2\}\text{Cl}_3]^-$ , with bipyridyl giving  $[\text{PtCl}_2(\text{bipy})]$  as final product has already been investigated [1, 2], and the formation of a 5-coordinate  $\pi$ -ethylene intermediate was postulated in both cases. Recently some of us have prepared and characterized a series of 5-coordinate  $\pi$ -ethylene platinum(II) complexes including  $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(\text{bipy})]$  [3] and we decided to study the kinetics of decomposition of this species in order to gain useful information on the mechanism of reaction of neutral bidentate ligands with complexes of type  $[\text{Pt}(\text{L}_\pi)\text{Cl}_3]^-$ .

### Experimental

#### Materials

The complex  $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(\text{bipy})]$  used in the reaction was prepared according to reported procedures [3]. All other materials were reagent grade products.

#### Kinetic Runs

The kinetics in 1,2-dichloroethane were studied by dissolving the solid substrate in the solvent placed in a thermostatted 1 cm path quartz cell and observing the absorbance changes in the U.V. region (400–250 nm) of the spectrum. The concentration of the starting complex was always  $\leq 5 \times 10^{-5} \text{ M}$ . First-order rate constants,  $k_{\text{obs}}$ , were obtained from semi-logarithmic plots of  $\ln(A_\infty - A_t)$  against time, where  $A_t$  and  $A_\infty$  are the absorbances at a given wavelength at time  $t$  and after 7–8 half-lives respectively. These plots were linear for at least 4 half-lives. The experimentally obtained rate constants and activation parameters are summarized in Table I (quoted uncertainties are estimated standard errors).

The kinetics in aqueous methanol relative to the first transformation,  $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(\text{bipy})] \rightarrow [\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}(\text{bipy})]^+ + \text{Cl}^-$ , were performed in a way that was completely analogous to that used for the runs in 1,2-dichloroethane. The solid substrate was directly dissolved in a solution of aqueous methanol (95% v/v) containing a known concentration of  $\text{LiClO}_4$ , which had been prethermostatted in a jacketed U.V. cell through which water circulated from a constant temperature bath at  $25.0 \pm 0.1^\circ \text{C}$ . By measuring the changes of absorbance vs. time the first-order rate constants were calculated as previously described. The data are affected by large errors since the kinetics are fast and the substrate dissolves with difficulty in this solvent, and are summarized in Table II.

The kinetics of the second change,  $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}(\text{bipy})]^+ + \text{Cl}^- \rightarrow [\text{PtCl}_2(\text{bipy})] + \text{C}_2\text{H}_4$ , in aqueous methanol were performed at  $25.0 \pm 0.1^\circ \text{C}$  and  $I = 0.2 \text{ M}$  using the following procedure. The solid substrate was dissolved in a thermostatted U.V. cell containing  $2 \text{ cm}^3$  of aqueous methanol and the first transformation followed spectrophotometrically. At the end of the first stage  $1 \text{ cm}^3$  of a solution of  $\text{LiCl}$  and  $\text{LiClO}_4$  in the same solvent, having a total

TABLE I. Values of Rate Constants,  $k_{\text{obs}}$ , at Different Temperatures for Reaction (1), and Corresponding Enthalpy and Entropy of Activation.

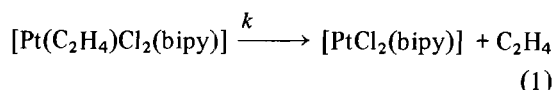
$t, ^\circ\text{C}$	$10^3 k_{\text{obs}}, \text{s}^{-1}$	$\Delta H^\ddagger,$ $\text{Kcal mol}^{-1}$	$\Delta S^\ddagger,$ $\text{cal K}^{-1}$ $\text{mol}^{-1}$
19.6	0.98		
29.9	3.20	$18.6 \pm 0.6$	$-8 \pm 2$
39.5	8.10		

concentration of 0.6 *M* and containing enough LiCl to achieve the desired  $[\text{Cl}^-]$  in the resulting solution, was added to the cell. From the changes of absorbance against time the pseudo-first-order rate constants were calculated as previously described. The results are summarized in Table II.

## Results and Discussion

### Reaction in 1,2-Dichloroethane

The spectral course of the reaction of decomposition of  $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(\text{bipy})]$  in 1,2-dichloroethane is shown in Figure 1. The presence from the beginning of two well defined isosbestic points at 292 and 310 nm clearly indicates that a single stage process takes place. The final spectrum corresponds to that of an authentic sample of  $[\text{PtCl}_2(\text{bipy})]$  in the same solvent, therefore the observed reaction is actually the release of ethylene from the 5-coordinate substrate and formation of the 4-coordinate complex [equation (1)].



The semilogarithmic plot of the variation of absorbance against time was linear for at least 4 half-lives indicating that the reaction rate is first-order in the complex concentration. Kinetic runs at different

TABLE II. Values of Rate Constants for Reaction (2),  $k_{\text{obs}}^{\text{I}}$ , and Reaction (3),  $k_{\text{obs}}^{\text{II}}$ , and Corresponding Kinetic Constants  $k^{\text{I}}$  and  $k^{\text{II}}$ .

$[\text{Cl}^-], ^a M$	$I, M$	$10^2 k_{\text{obs}}^{\text{I}}, \text{s}^{-1}$	$10^5 k_{\text{obs}}^{\text{II}}, \text{s}^{-1}$	$k^{\text{I}}, \text{s}^{-1}$	$k^{\text{II}}, M^{-1}\text{s}^{-1}$
0.00	0.02	1.99	}	$1.93 \times 10^{-2}$	}
0.00	0.04	1.89			
0.00	0.10	1.91			
0.00	0.20	1.95			
0.04	0.20		1.32	$3.20 \times 10^{-4}$	
0.10	0.20		3.16		
0.16	0.20		4.80		
0.20	0.20		6.36		

<sup>a</sup> Excess chloride ion added.

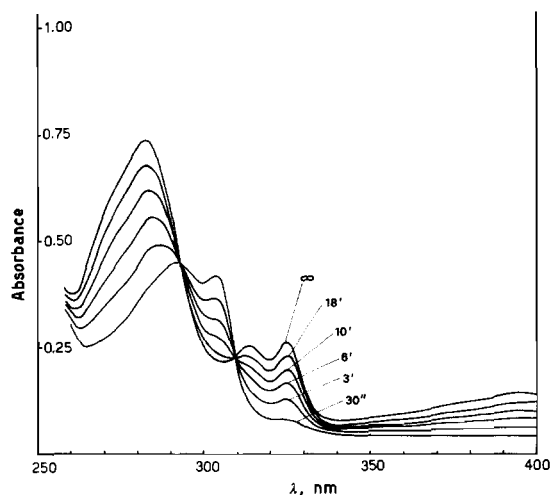
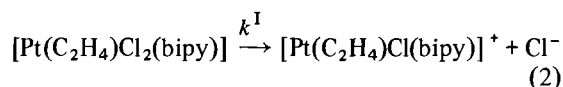


Fig. 1. Spectral changes for the reaction  $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(\text{bipy})] \rightarrow [\text{PtCl}_2(\text{bipy})] + \text{C}_2\text{H}_4$  in 1,2-dichloroethane. Complex conc. ca.  $5 \times 10^{-5} M$ .

temperatures were performed in order to estimate the values of the activation parameters  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$ ; they were found to be  $18.6 \pm 0.6 \text{ Kcal mol}^{-1}$  and  $-8 \pm 2 \text{ cal K}^{-1} \text{ mol}^{-1}$ . These values are not in disagreement with a dissociative mechanism although no direct comparison with other data concerning the decomposition of 5-coordinate substrates in non-coordinating solvents is feasible [4].

### Reaction in Aqueous Methanol

In aqueous methanol the 5-coordinate  $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(\text{bipy})]$  complex undergoes a fast chemical transformation whose final spectrum (curve B in Fig. 2) does not correspond to that of  $[\text{PtCl}_2(\text{bipy})]$  (curve C in Fig. 2) and has been assigned to a cationic species of formula  $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}(\text{bipy})]^+$  [equation (2)] [1].



Analogous cationic complexes have been isolated

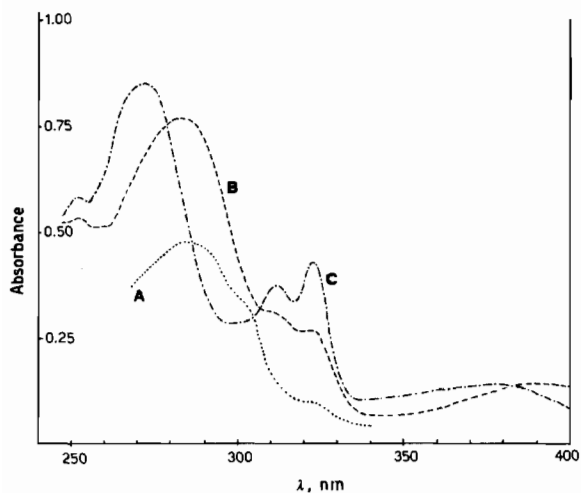
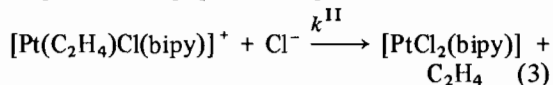


Fig. 2. A) Spectrum of  $[Pt(C_2H_4)Cl_2(bipy)]$  in aqueous methanol solution taken soon after dissolution (by which time some  $[Pt(C_2H_4)Cl(bipy)]^+$  is formed). B) Spectrum of the cationic intermediate  $[Pt(C_2H_4)Cl(bipy)]^+$  at the end of reaction (2). C) Spectrum of the final product  $[PtCl_2(bipy)]$  at the end of reaction (3). Complex conc. ca.  $5 \times 10^{-5} M$ .

with acetylenes in place of ethylene [5]. In absence of added  $Cl^-$  and with a complex concentration  $\leq 5 \times 10^{-5} M$ , the cationic species remains unchanged after several hours; however, if chloride ion is added to the solution a slow process takes place and  $[PtCl_2(bipy)]$  is formed [equation (3)].



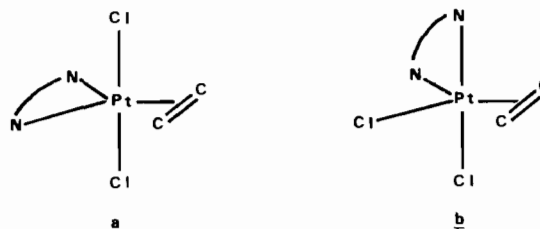
The spectral changes relative to this second process are shown in Figure 2 (curves B and C). The presence of three isosbestic points (in the range 400–250 nm) at 297, 306, and 384 nm clearly indicates that this is a single stage process. The rate of this second process has been measured and found to be first-order in the substrate and entering chloride.

Reaction (2) probably occurs through a dissociative mechanism analogous to that suggested for reaction (1), the only difference being that in aqueous methanol chloride is displaced in preference to ethylene. The nature of the solvent plays an important role in determining which group will dissociate first from the 5-coordinate substrate. In a solvent such as 1,2-dichloroethane with low dielectric constant and poor coordinating ability a process leading to formation of neutral species is preferred; in aqueous methanol (a solvent with high dielectric constant and good coordinating ability) a process leading to formation of two ionic species is preferred instead. We cannot exclude that in addition to reaction (2) also reaction (1) could occur in methanol, but on comparing the relative rates of the

two processes it appears that reaction (2) is by far the more favoured in methanol. We have measured the rate of reaction (2) at different ionic strength and it has been found to be constant within experimental error.

Reaction (3) has been found to occur through the associative mechanism usually found in square-planar substrates. The solvolytic pathway, however, has not been detected and the reaction rate has been found to be proportional to the chloride ion concentration.

The transition state in reaction (3) should again be a 5-coordinate  $\pi$ -ethylene species having the same stoichiometry as the starting 5-coordinate substrate. However, the arrangement of the ligands around the platinum atom might be different. In fact, whereas the starting substrate is likely to have configuration a (based on an X-ray structure determination for an analogous complex [6]), according to general theories [4] the activated intermediate of reaction (3) should have configuration b:



The main difference between the present kinetic data and those reported for direct reaction of Zeise's salt with bipyridyl concerns the rate of reaction (3). In fact, contrary to a previous report, we found a reaction rate proportional to the chloride ion concentration. The explanation for this disagreement has been found on performing an experiment in which the 5-coordinate complex was allowed to decompose in a water-methanol solution containing chloride ion right from the beginning. Under these circumstances a completely different reaction course is observed. In fact, in addition to the pathway leading first to the formation of the cationic intermediate [equation (2)] and then to  $[PtCl_2(bipy)]$  [equation (3)], a second reaction pathway, also leading to  $[PtCl_2(bipy)]$  as final product, but proceeding through a different intermediate, is observed. The two different pathways are parallel and until now no kinetic data for this second path have been obtained. We are still pursuing our investigations in order to clarify the nature of this second path.

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