Journal of Organometallic Chemistry, 113 (1976) 91—97

REACTIONS AND PROPERTIES OF SOME TRIMETHYLENEPLATINUM(IV) COMPLEXES

III *. THE MECHANISM OF THERMAL DECOMPOSITION IN SOLUTION

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(Received January 12th, 1976)

Summary

The thermal decomposition of the compounds, $PtX_2(C_3H_6)(L—L)$ (where $X = Cl, Br$; $L—L$ = 2,2′-bipyridine, 1,10-phenanthroline) in solution has been followed by UV spectrophotometry. The products of reductive elimination are $PtX_2(L—L)$ and cyclopropane (with some propene) and the reaction is first order in the trimethylene compounds, the rate being little affected by added halide but markedly reduced by small amounts of added 2,2′-bipyridine. A simple mechanism, involving an initial reversible dissociation of the bidentate ligand, is suggested.

Introduction

The preparation, structure and reactions of trimethyleneplatinum(IV) compounds have been extensively studied [1,2], and the results of an investigation of the thermal decomposition in the solid phase have been reported [3]. The first step appears to be the elimination of the C_3H_6 moiety as a mixture of cyclopropane and propene, but the kinetic data (obtained by an isothermal differential scanning calorimetric technique) were difficult to interpret. We have now investigated the homogeneous decomposition of the compounds $PtX_2(C_3H_6)(L—L)$ (where $X = Cl, Br$; $L—L$ = 2,2′-bipyridine, 1,10-phenanthroline) in solution. The nitrogen ligands were chosen because the progress of the reaction can be followed simply by UV spectrophotometry.

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[*] For part II, see ref. 1.

Results and discussion

The trimethyleneplatinum(IV) compounds in solution in *o*-dichlorobenzene decompose at about 130°C to give the corresponding platinum(II) compounds, with loss of the C_3H_6 moiety mostly as cyclopropane (75—85%), the remainder being propene (eq. 1). Decomposition in solution gave considerably more cyclopropane compared with propene than decomposition of the solids [3] when only 36—40% cyclopropane was formed under similar conditions.

$$[\mathrm{PtX_2(C_3H_6)(L{-}L)}] \rightarrow [\mathrm{PtX_2(L{-}L)}] + \overline{\mathrm{CH_2CH_2CH_2}} \qquad (1)$$

The platinum(IV) compounds in solution do not absorb radiation of wavelengths longer than 325 nm whereas the platinum(II) products have a band in the absorption spectrum centred at ~412 nm in each case [4]. The final UV spectrum was identical with that of $[\mathrm{PtX_2(L{-}L)}]$ in each case. Thus, the progress of the reaction was followed by removing samples of the thermostatted solution after various times and measuring the absorption spectrum. The peak centred at ~412 nm grew as the decomposition proceeded (Fig. 1) and the values of $(A_\infty - A_t)$, where A_t is the absorbance (411 nm) at time t and A_∞ the absorbance when the reaction was complete (determined by extrapolation, from the A_t values, if necessary), are proportional to the concentration of the platinum(IV) compound remaining (see the stoichiometry).

It was found that the rate of decomposition depended markedly on the nature of the solvent, e.g., mesitylene << chlorobenzene < *o*-dichlorobenzene. Most of the kinetic data were obtained using *o*-dichlorobenzene, since it has a suitably high boiling point and there were no appreciable side reactions. The 1,10-phenanthroline(trimethylene)platinum(IV) compounds decomposed very slowly in this solvent, even at about 130°C, but the decomposition of the 2,2'-bipyridine compounds was much faster and could be followed conveniently. The

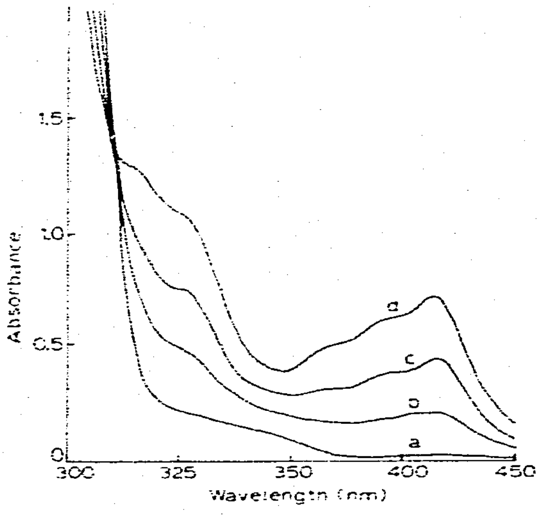


Fig. 1. Changes in the UV spectrum during the decomposition of $[\mathrm{PtBr_2(C_3H_6)(bipy)}]$ in *o*-dichlorobenzene at 130°C in the presence of 2,2'-bipyridine (1.8×10^{-5} *M*). (a) t = 0; (b) t = 30 min; (c) t = 80 min; (d) infinity (24 h).

reaction was first order, and some typical plots of $\log(A_\infty - A_t)$ versus time are shown in Fig. 2. The rate coefficients were reasonably reproducible (±5%) with compound from the same preparation but different samples gave less reproducible data, due probably to the difficulty of removing all traces of free 2,2'-bipyridine which is a very powerful retarder (see below). Typical data are given in Table 1.

The rate coefficient for decomposition of the chlorine compound is about three times greater than that for the bromine compound at 123°C in *o*-dichlorobenzene (Fig. 2) and the overall activation of decomposition of the former, from the Arrhenius plot (Fig. 3), is approximately 196 kJ mol^{-1}.

Whereas added tetramethylammonium chloride had little effect on the rate of decomposition of $[PtCl_2(C_3H_6)(bipy)]$, added 2,2'-bipyridine retarded the reaction with both the chlorine and the bromine compounds very markedly, the reciprocal of the rate coefficient observed being linearly related to the concentration of additive (Fig. 4). With the small concentrations of added bipyridine used no interaction with starting material or products took place as shown by independent studies. This strongly suggests that the first step in the decomposition is loss of the 2,2'-bipyridine rather than isomerization to give ion-pairs [1,3], a likely simple reaction mechanism being shown in Scheme 1 (S = solvent):

SCHEME 1

$$[PtX_2(C_3H_6)(bipy)] + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [PtX_2(C_3H_6)S] + bipy \qquad (a)$$

(C) (I)

$$[PtX_2(C_3H_6)S] \xrightarrow{k_2} [PtX_2 \cdot S] + \overline{CH_2CH_2CH_2} \qquad (b)$$

$$[PtX_2 \cdot S] + bipy \xrightarrow{fast} [PtX_2 \cdot bipy] + S \qquad (c)$$

The rate of decomposition:

$$-d[C]/dt = k_1[C][S] - k_{-1}[I][bipy]$$

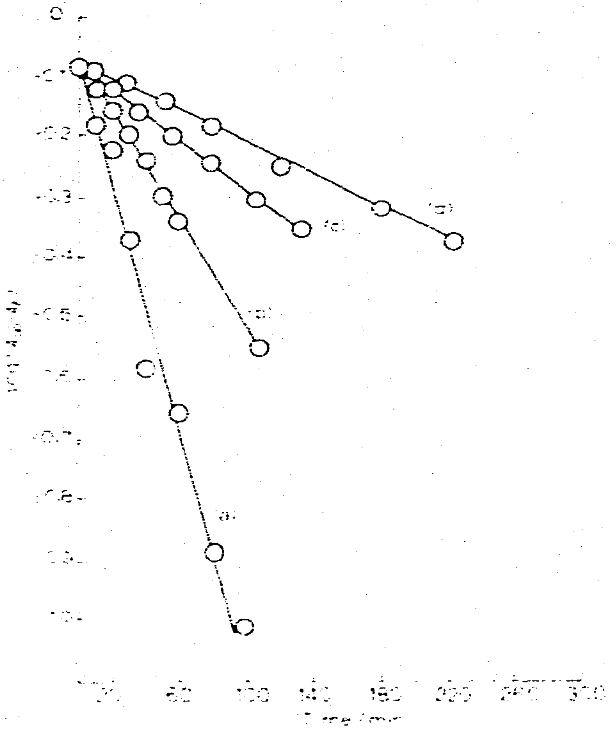
Assuming a stationary concentration of the labile intermediate I, we have

$$k_1[C][S] = k_{-1}[I][bipy] + k_2[I]$$

TABLE 1

FIRST ORDER RATE CONSTANTS, k, FOR THE DECOMPOSITION OF $[PtX_2(C_3H_6)(bipy)]$

X	T(°C)	Solvent	k (sec^{-1})
Cl	117	chlorobenzene	1.32×10^{-5}
Cl	123	chlorobenzene	2.95×10^{-4}
Br	123	chlorobenzene	1.97×10^{-4}
Cl	110	*o*-dichlorobenzene	6.14×10^{-5}
Cl	117	*o*-dichlorobenzene	1.75×10^{-4}
Cl	123	*o*-dichlorobenzene	3.94×10^{-4}
Br	123	*o*-dichlorobenzene	1.38×10^{-4}



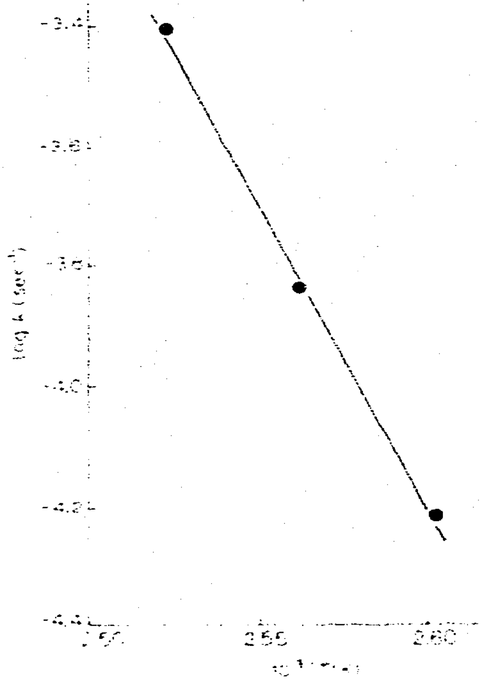


Fig. 2. First order plots for the decomposition of [$PtX_2(C_3H_6)$(bipy)] in o-dichlorobenzene at 130 °C. (a) X = Cl, [bipy] = 0; (b) X = Br, [bipy] = 0; (c) X = Cl, [bipy] = 1.3×10^{-5} M; (d) X = Cl, [bipy] = 1.56×10^{-5} M.

Fig. 3. Arrhenius plot for the decomposition of [$PtCl_2(C_3H_6)$(bipy)] in o-dichlorobenzene.

Thus,

$$-d[C]/dt = k_2[I] = k_1k_2[C][S]/(k_{-1}[\text{bipy}] + k_2)$$

The concentration of solvent remains constant, and assuming that reaction c is very fast, so will the concentration of 2,2'-bipyridine. Thus the process if first order, the observed rate coefficient, k_{obs}, being:

$$k_{obs} = k_1k_2[S]/(k_{-1}[\text{bipy}] + k_2)$$

Inverting this equation we have:

$$1/k_{obs} = k_{-1}[\text{bipy}]/k_1k_2[S] + 1/k_1[S]$$

which is a linear relationship between the reciprocal of the observed rate coefficient and the 2,2'-bipyridine concentration. For [$PtCl_2(C_3H_6)$(bipy)] at 30 °C in dichlorobenzene this gives $k_{-1}/k_1k_2[S] = 1.1 \times 10^{4}$ l mol^{-1} sec and $1/k_1[S] \doteq 2700$ sec. The overall activation energy cannot be associated with any particular elementary step.

The initial loss of a bidentate ligand seems unusual, but the detachment of one nitrogen only with possible attachment of a second 2,2'-bipyridine molecule (acting as a unidentate ligand) seems most improbable on steric grounds

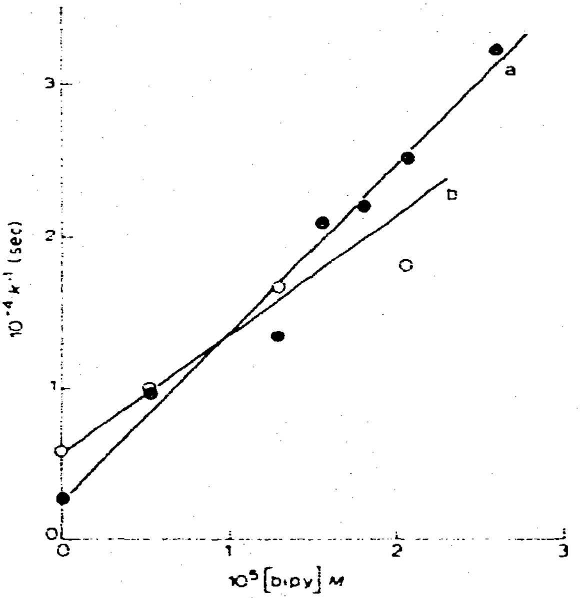


Fig. 4. Dependence of $1/k$ (where k is the first order rate constant for decomposition of [$PtX_2(C_3H_6)$-(bipy)] in *o*-dichlorobenzene at 130°C) on the concentration of added 2,2′-bipyridine. (a) X = Cl; (b) X = Br.

and would be inconsistent with the kinetics in the presence of added 2,2′-bipyridine; also added pyridine has no appreciable effect on the rate. The retarding effect of 2,2′-bipyridine has been noted recently with other systems, e.g. in the reaction of diethyl(2,2′-bipyridine)platinum(II) with methyl acrylate where the initial step was displacement of 2,2′-bipyridine from platinum by methyl acrylate [5].

The reaction may also be compared with the reductive elimination of ethane from *fac*-[$PtIMe_3(PMe_2Ph)_2$] which takes place after preliminary dissociation of a phosphine ligand, though the similar complex *fac*-[$PtIMe_3$(diphos)] with the ligand diphos = $Ph_2PCH_2CH_2PPh_2$ decomposed without prior dissociation of the chelate ligand [6]. Possible reasons for enhanced reactivity towards reductive elimination in the co-ordinatively unsaturated intermediates formed by ligand dissociation have been discussed previously [6].

It is also interesting that the reaction gives predominantly cyclopropane by simple reductive elimination, probably via an intermediate cyclopropaneplatinum(II) "edge complex" [2,7,8], rather than propene formed by initial β-elimination to give a (π-allyl)hydridoplatinum(IV) intermediate which then undergoes reductive elimination to give propene [3]. Decomposition of tetramethyleneplatinum(IV) complexes yields no cyclobutane but only but-1-ene [9]. Thus it seems that reactivity in the trimethyleneplatinum(IV) complexes is greater towards reductive elimination (possibly because the intermediate edge-complex is fairly stable [7]) but lower towards β-elimination (possibly because of the rigidity of the 4-membered ring which makes it difficult for platinum to interact with the β-hydrogen atoms) compared with the tetramethylene compounds.

The products of decomposition may also be compared with those from [$PtCl_2(C_3H_6)py_2$], py = pyridine, which gave the ylid complex [$PtCl_2${CH(Et)-

py ; py], formed by attack of pyridine on the intermediate $[PtCl_2(C_3H_6)py]$ formed by dissociation of pyridine from the starting material [10]. No evidence for long-lived intermediates was obtained on decomposition of the 2,2′-bipyridine and 1,10-phenanthroline complexes in the present work so that, as would be expected for chelate complexes, ylid formation does not take place in these reactions. Gillard in his studies of the kinetics of formation of the ylid complex noted that the intermediate $[PtCl_2(C_3H_6)py]$ could eliminate C_3H_6 in a minor reaction. He suggested an intermediate formed by heterolysis of a Pt—C bond, $[(py)Cl_2\overset{+}{Pt}CH_2CH_2\overset{-}{C}H_2]$, which then eliminated cyclopropane [10]. We believe that the concerted mechanisms of decomposition proposed by us are more likely, since the rearrangement of a ring-opened intermediate as suggested by Gillard to give the strained-ring cyclopropane is unlikely.

Experimental

$[PtCl_2(C_3H_6)(bipy)]$ and $[PtBr_2(C_3H_6)(bipy)]$ were prepared as described earlier.

$PtCl_2(C_3H_6)(1,10$-phenanthroline)

Solutions of $[PtCl_2(C_3H_6)py_2]$ (0.27 g) in dichloromethane (10 cm^3) and 1,10-phenanthroline (0.10 g) in dichloromethane (5 cm^3) were mixed. After two h at room temperature in the dark (to avoid photolysis), the white crystals of the product were filtered off, washed with dichloromethane and dried under vacuum. Yield 61%. It decomposed without melting at 224°C. Analysis found: C, 37.3; H, 2.5; N, 5.75. $C_{15}H_{14}Cl_2N_2Pt$ calcd.: C, 36.9; H, 2.9; N, 5.7%.

Product analysis

Decomposition was carried out at 130°C in *o*-dichlorobenzene and the volatile products were condensed in a trap cooled in liquid nitrogen. The trap was isolated and allowed to warm to room temperature. The cyclopropane and propene were then estimated by GLC as described earlier. $[PtCl_2(C_3H_6)(bipy)]$ gave 85% cyclopropane, 15% propene and $[PtBr_2(C_3H_6)(bipy)]$ gave 75% cyclopropane and 25% propene. The complexes $[PtX_2(L{-}L)]$ X = Cl, Br; L—L = 2,2′-bipyridine, 1,10-phenanthroline crystallised from solution on cooling and were identified by UV and IR spectra.

Kinetics

The redistilled solvent (50 cm^3) was preheated to the required temperature using a refluxing organic liquid (toluene for 110°C, n-butanol for 117°C, n-octane for 123°C and chlorobenzene for 130°C) to provide a constant temperature. The complex (5—7 mg) was then added to give a concentration of about 2×10^{-4} *M* and samples were withdrawn at suitable intervals for UV analysis. UV spectra were recorded using a Unicam SP800 spectrophotometer. The rates in mesitylene solvent were too low for kinetic studies. Care was taken to exclude light since the trimethyleneplatinum(IV) complexes are somewhat photosensitive. For decomposition of $[PtBr_2(C_3H_6)(bipy)]$ an isosbestic point was found at 312 nm in the UV spectrum, indicating that the reaction proceeded without formation of long-lived intermediates. No cross-over in the UV spectra occurred for decomposition of $[PtCl_2(C_3H_6)(bipy)]$.

The very dilute solutions of 2,2′-bipyridine in *o*-dichlorobenzene (0—3×10^{-5} *M*) were prepared by dilution of a more concentrated stock solution as required. Higher concentrations of added bipyridine gave rate constants too low to measure satisfactorily.

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