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PROGRAMMED PROBE THERMAL ANALYSIS AND ITS USE IN THE STUDY OF THERMAL DECOMPOSITION OF SOME *trans*-SUBSTITUTED DERIVATIVES OF ZEISE'S SALT

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ABSTRACT

A mass spectrometer equipped with a programmed probe and a total ion monitor may be used to study thermal decompositions by gradually heating the sample in the probe. The ion current is monitored and mass spectra taken at appropriate points permit the identification of decomposition products. Single ion monitoring can also be employed. The method has been used to examine a series of compounds formed by the replacement of the *trans*-Cl ligand of Zeise's salt. Pathways for the thermal decomposition are postulated.

INTRODUCTION

One of the major disadvantages in the use of thermogravimetric analysis (TGA) for the study of thermal decomposition of organometallic compounds is that the data obtained cannot be used to positively identify the decomposition products. This drawback may be overcome by coupling a gas chromatograph (GC)[1] or a mass spectrometer (MS)[2] or even the more powerful combination of the two (GC–MS)[3] directly to the TGA apparatus. The use of chemical ionization-MS has also been reported[4]. Techniques employing GC or GC–MS can be used to identify the products by their retention times and/or mass spectra, but provide no information on the temperature at which the products were evolved. This can be achieved either by directly monitoring the effluent gases of the TGA apparatus with a mass spectrometer or by inference from the TG data.

In laboratories which do not possess such advanced techniques, the problem of the identification of products may be approached in another way if GC–MS is available: by heating the sample in a furnace at the injection port of the GC instrument. This has been the approach in our laboratories recently[5]. Previously, the temperature relationship has been obtained by heating the sample in a programmable furnace inside a mass spectrometer[6, 7].

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A simpler way, however, is to heat the sample at a known rate, in the direct insertion probe of a mass spectrometer. With due regard to ionization efficiencies, the total ion monitor (TIM) output is proportional to the amount of gas evolved. It thus becomes possible to relate the TIM output and the mass spectra to events in the TG data.

Programmed Probe Analysis

The JEOL JMS D100 mass spectrometer can be equipped as an optional extra, with a direct probe whose temperature can be increased at a programmed rate between −100 °C and +400 °C. Six programme rates are available. This instrument is also equipped with a total ion monitor. In use, a small sample (about 0.1 mg) is gradually heated, usually at 5 °C min^{-1} and the total ion current output recorded. Mass spectra can be taken as appropriate or a second pen on the TIM recorder can be used to monitor a particular *m/e* value. A third pen on the recorder indicates probe temperature.

Zeise's Salt Derivatives

The chloride ligand trans to ethylene in the anion of Zeise's salt, $[(C_2H_4)PtCl_3]^-$, can easily be replaced with a variety of ligands[8−10], yielding a series of complexes of general formula $(C_2H_4)PtCl_2$. L. Iwayanagi and Saito employed the ligands pyridine (py), 4-methylpyridine ($4\text{-}CH_3\text{–py}$), pyridine-N-oxide (py–NO), 4-methylpyridine-N-oxide ($4\text{-}CH_3\text{–py–NO}$) and dimethylamine in magnetic resonance studies[11] because these ligands exhibit a range of trans influences upon the Pt–ethylene bond. It was our intention to use these same ligands to investigate whether any marked changes resulted in the mechanism of thermal decomposition of the complexes. The methods employed to characterize the thermal decompositions were thermogravimetric analysis (TG), pyrolysis–evolved gas analysis (P–EGA) and the programmed probe thermal analysis described herein.

EXPERIMENTAL

Zeise's salt was prepared by the method of Halpern and co-workers[12] and the *trans* chloride ligand replaced by slow addition with rapid stirring of a solution of the replacing ligand in ethanol to an equimolar quantity of Zeise's salt dissolved in water. The products obtained were recrystallized from AR acetone.

Microanalyses were carried out by the Australian Microanalytical Service, C.S.I.R.O. and confirmed the identity of the complexes.

Simultaneous TG, DTG and DTA curves were recorded on a Rigaku-Denki Thermoflex Desktop TG–DTA thermobalance, for all complexes prepared. Samples were all approximately 10 mg, and a similar amount of aluminium oxide was used as a reference material. Sample holders were 5 × 5 mm diameter silica crucibles and measurements were carried out in nitrogen and static air atmospheres, from room temperature to 600 °C. Heating rates were either 10 °C or 20 °C min^{-1}. (The faster heating rates tend to amplify DTG signals). Preliminary runs were carried out both in

TABLE I

THERMOGRAVIMETRIC ANALYSES

L	*Heating rate* (°C min^{-1})	*Temp. range of mass loss*	*Wt. loss A–B* (%)	*Expected*[a] *wt. loss*	*Δ*	*Temp. range of mass loss*	*Wt. loss B–C* (%)	*Expected*[b] *wt. loss*	*Δ*
py	10	120–300	28.74	28.72	+0.02	300–480	24.84	26.67	−1.83
	20	120–300	30.44	28.72	+1.72	300–500	25.51	26.67	−1.16
py-NO	10	140–350	32.23	31.65	+0.58	350–460	25.34	26.67	−1.33
	20	130–410	24.57	31.65	−7.08	410–540	23.09	26.67	−3.58
4-CH_3-py	10	140–360	26.58	31.31	−4.47	360–440	28.19	26.67	+1.52
	20	120–370	26.93	31.31	−4.38	370–470	23.95	26.67	−2.72
4-CH_3-py-NO	10	150–300	33.10	34.19	−1.09	300–440	24.82	26.67	−1.85
	20	150–320	30.92	34.19	−3.27	320–460	24.01	26.67	−2.66
$HN(CH_3)_2$	10	110–360	37.25	42.48	−5.23				
	20	110–300	34.24	42.48	−8.24				
Zeise's salt	10	44–420	38.65	39.43	−0.79				
	20	62–560	37.66	39.43	−1.77				

[a] Expected value based on step (1) (except for Zeise's Salt and $HN(CH_3)_2$ complex in which both steps merge).

[b] Expected value based on step (2).

air and in nitrogen, to determine if oxidation was occurring, but no oxidative processes were apparent from TG curve comparisons. On the basis of this result, all following studies were performed in a static air atmosphere.

RESULTS

Thermoanalytical curves for the complexes in which L = py, py–NO, 4-CH$_3$–py and 4-CH$_3$–py–NO were quite similar and are exemplified by the data for the pyridine complex given in Fig. 1. Similar data for the other complexes is summarized in Table 1. The curves for the complex with L = HN(CH$_3$)$_2$ and Zeise's salt itself are rather different and are shown in Figs. 2 and 3 respectively. In all cases, decomposition of the complexes apparently occurs in two overall steps. The first overall step is not a smooth loss, as seen from the TG curve inflection and as reflected in the DTG curve. The results in Table 1 indicate that the overall TG processes correspond largely to the two decomposition steps

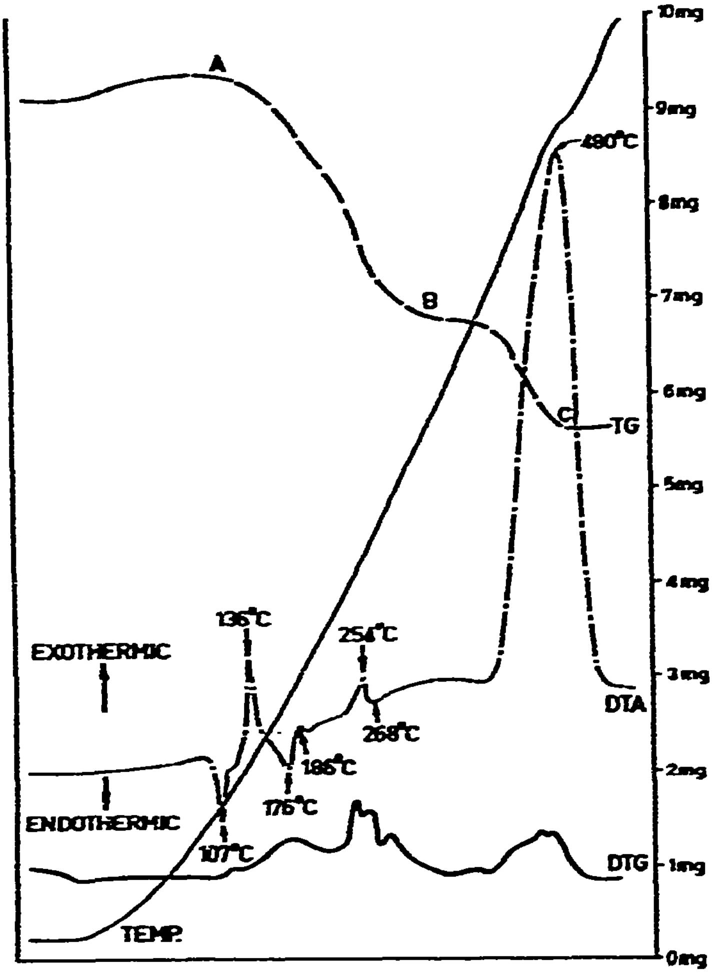

Fig. 1. TG/DTA/DTG plots for (C$_2$H$_4$)PtCl$_2$ · NC$_5$H$_5$.

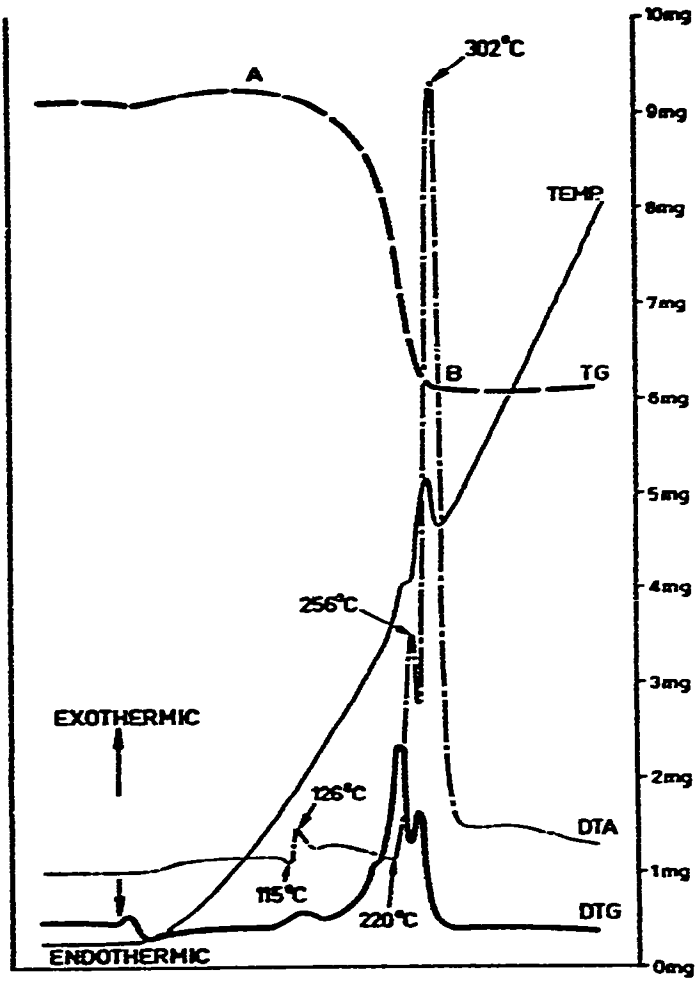

Fig. 2. TG/DTA/DTG plots for $(C_2H_4)PtCl_2NH(CH_3)_2$.

$$(C_2H_4)PtCl_2.L \rightarrow PtCl_2 + CH_2{=}CH_2 + L \quad (1)$$
$$PtCl_2 \rightarrow Pt + 2Cl^{\cdot} \quad (2)$$

For Zeise's salt (Fig. 3), the mass loss A–B corresponds to the loss of all ligands and coordinated water.

Curves obtained from the programmed probe thermal analysis of the complex with L = 4-CH_3–py–NO are given in Fig. 4.

The total ion current curve indicates three major losses; the first, and largest, occurring at ca. 150°C, the other two occurring at ca. 225°C and ca. 260°C. Corresponding to the first loss, maxima are also noted in the *m/e* = 28, 36, 109 and 387 curves. The presence of the *m/e* = 387 peak indicates the possibility that some proportion of all other peaks is due to mass-spectral fragmentation of this ion. For the other two peaks in the total ion current curve, only HCl appears to be evolved (*m/e* = 36).

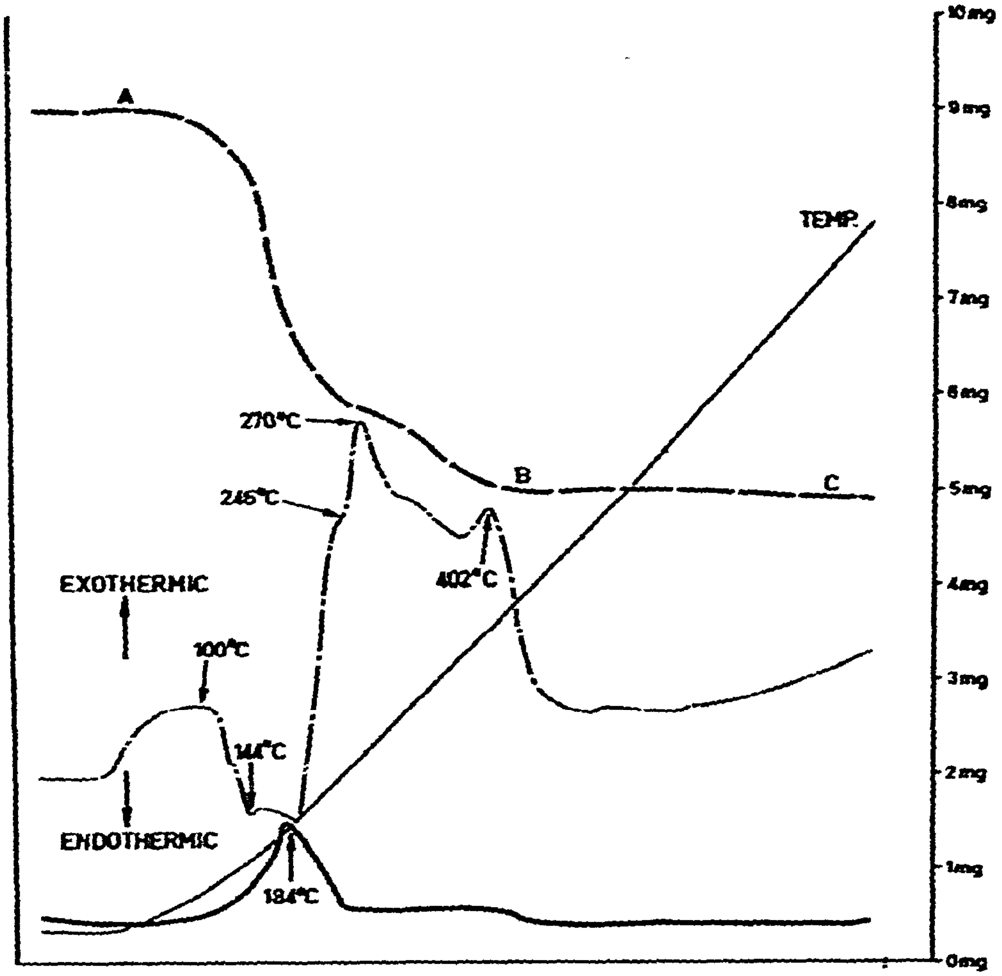

Fig. 3. TG/DTA/DTG plots for Zeise's salt.

Programmed probe thermal analysis curves for the complexes in which L = py, py–NO and 4-CH_3–py are similar to those for the 4-CH_3–py–NO complex, varying only in the *m/e* values monitored. A summary is presented in Table 2.

For the complex in which L = $HN(CH_3)_2$, the total ion current indicates three losses during decomposition: at 70°, 100° and 140°C (Fig. 5). It is evident that *m/e* = 45 and *m/e* = 28 are lost simultaneously, while *m/e* = 36 is lost independently of all other ions.

For Zeise's salt, the plot presented in Fig. 6 is extremely simple, compared with those for other complexes. This is probably due to the lack of variation of the ligands. From this plot, the total ion current curve indicates two major losses, occurring at 165°C and 200°C, the latter loss having a broad tail, extending to 250°C.

The *m/e* = 28 curve corresponds to the total ion current curve in the 165°C and 200°C regions, while the *m/e* = 36 responds to the 200°C region as well as to the broad tail region, 250°C.

On analysis of the thermograms for the complexes in which L = 4-CH_3–py–NO

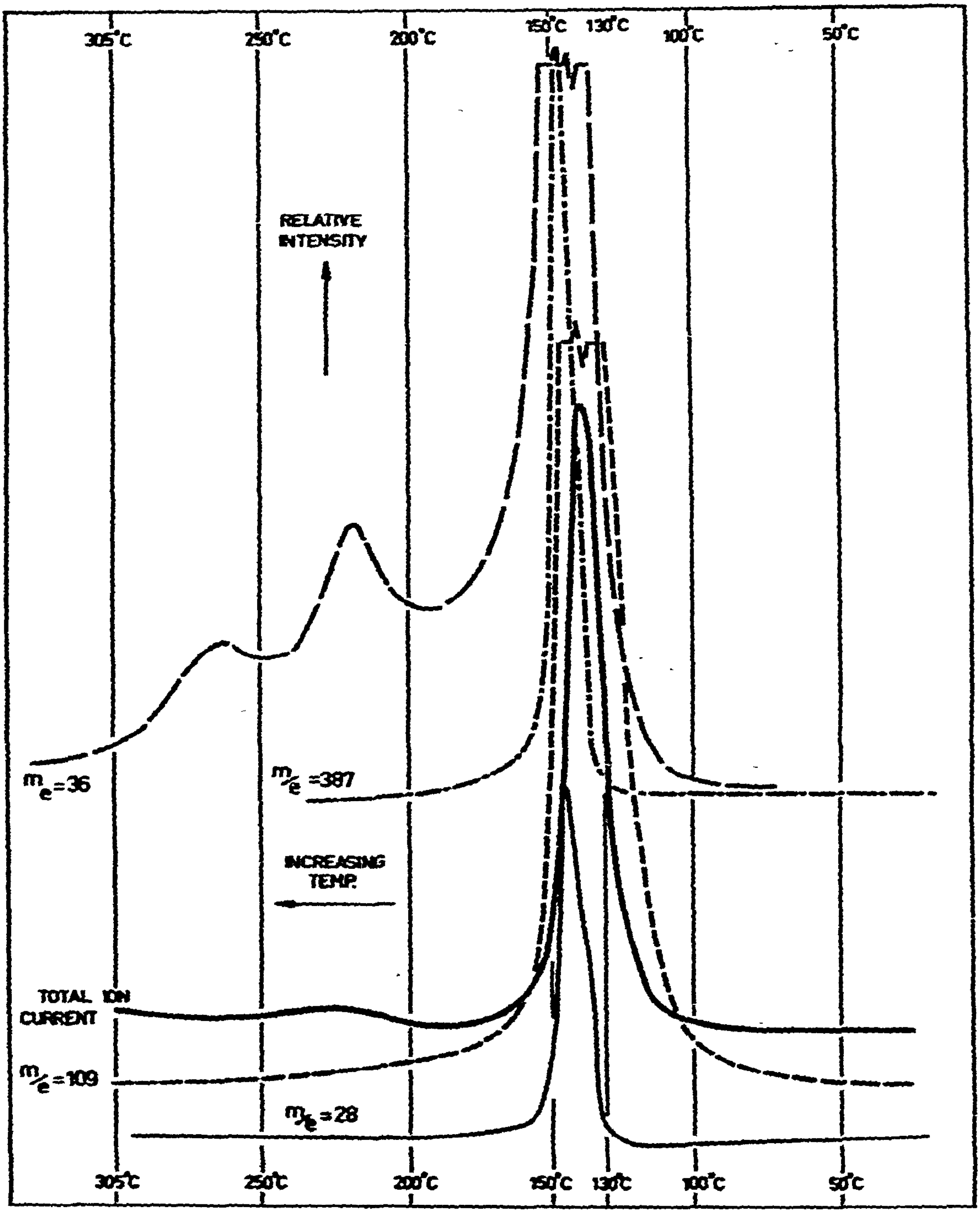

Fig. 4. Results of the programmed probe analysis for the 4-CH_3-py-NO complex.

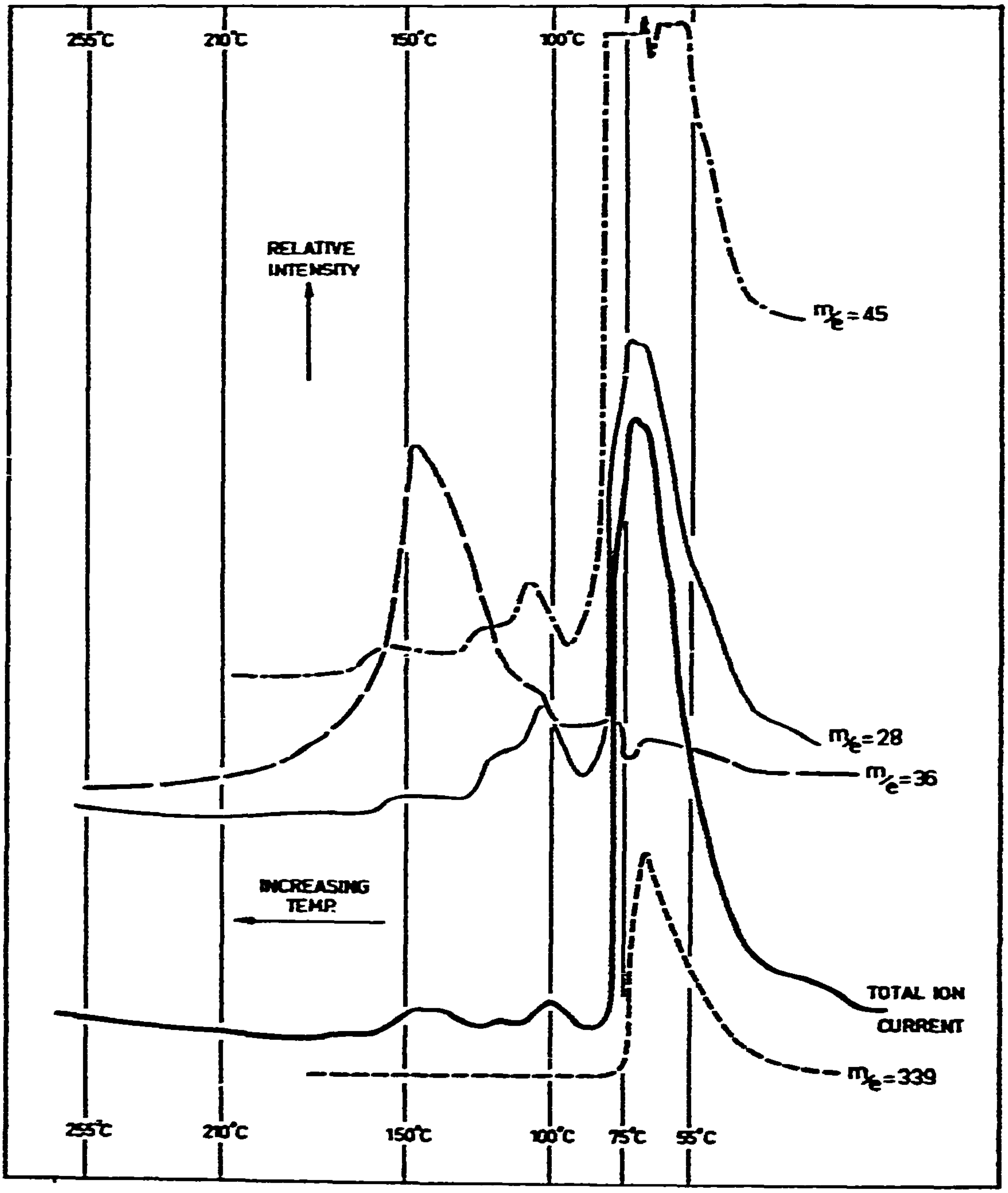

Fig. 5. Results of the programmed probe analysis for the $HN(CH_3)_2$ complex.

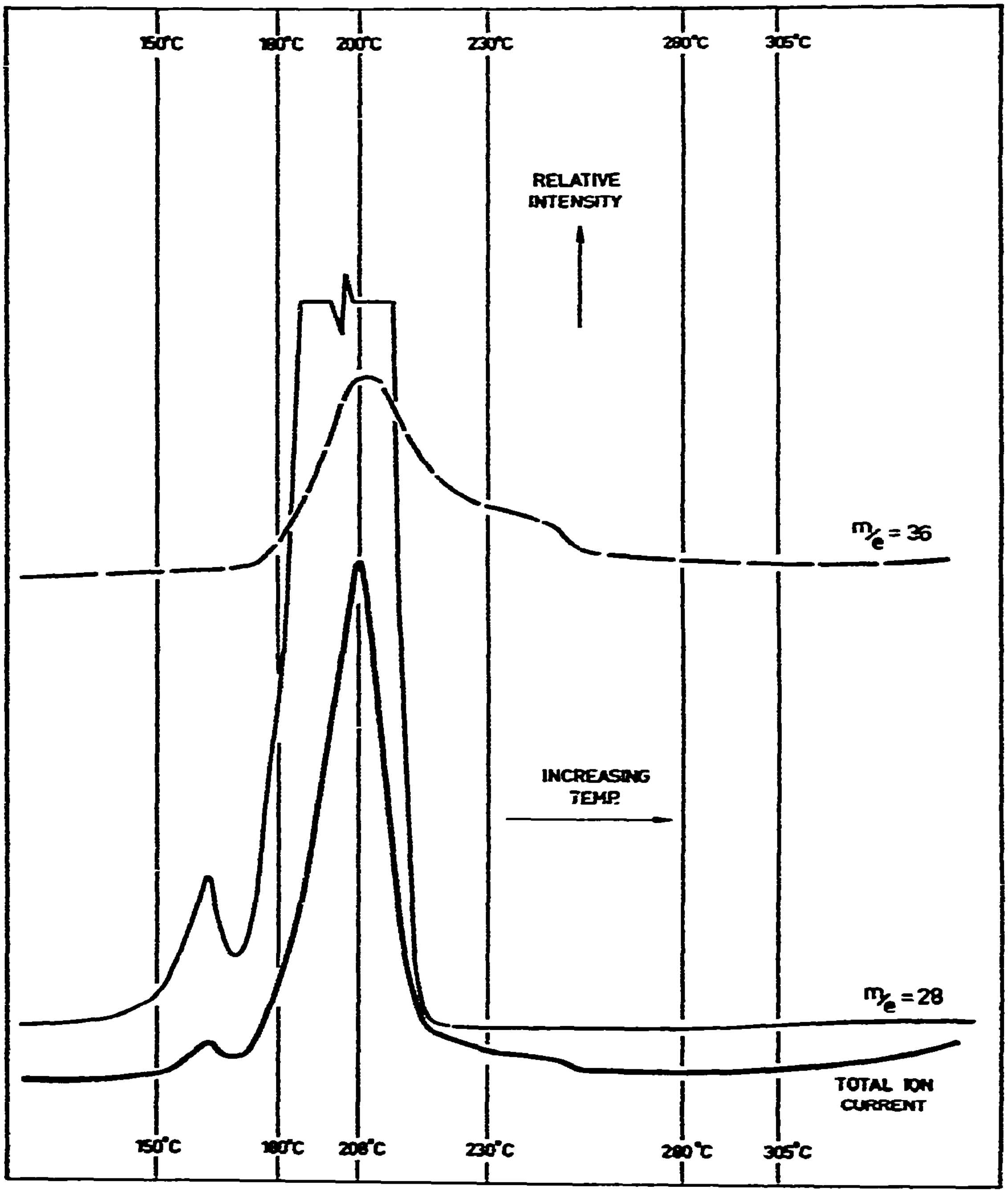

Fig. 6. Results of the programmed probe analysis for Zeise's salt. (Note that the temperature scale runs in the direction opposite to that given in Figs. 4 and 5.)

TABLE 2

RESULTS OF PROGRAMMED PROBE THERMAL ANALYSIS

Ligand denoting complex	*Peak temperature*[a] *(°C)*	*m/e value of fragment detected*
4-CH_3-py-NO	140	28, 36, 93, 109, 387
	220	36, 93
	260	36, 93, 451
py-NO	140	28, 36, 79, 95, 372
	180	36, 79
	260	36, 79, 423
py	110	28, 36, 79, 373
	160	28, 36, 79, 373
	240	36, 79, 423
4-CH_3-py	100	28, 36, 93, 387
	130	36, 93
	230	36, 93, 450
DMA	70	36, 28, 45, 339
	110	36, 28, 45
	150	36
Zeise's Salt	160	28
	200	28, 36
	230	36

[a] Peak temperatures are only approximate, in that many of the fragments detected came off at slightly higher or lower temperature. This fact is important in terms of mechanistic studies.

and dimethylamine, calculated and expected weight losses disagreed by up to 8%, the greatest discrepancy being for the dimethylamine complex. Consequently 100 mg samples of the dimethylamine and 4-CH_3-py-NO complexes were pyrolyzed by programmed heating on the thermobalance, then holding the temperature steady at 560°C for one hour, after which the residue was cooled and microanalyzed. The results are presented below.

	Found (%)				
L	*C*	*H*	*N*	*Cl*	*O*
$NH(CH_3)_2$	<0.4	<0.1	<0.1	<0.3	–
4-CH_3-py-NO	<0.1	<0.1	<0.1	<0.3	0.4

Obviously, most of each residue was platinum metal although detectable amounts of other elements were present.

DISCUSSION

The results from the thermogravimetric experiments show that while the results can be satisfactorily analyzed in terms of the two steps suggested above, the curve shapes and the two pyrolysis experiments indicate that the system is far from being straightforward. The thermal decomposition proceeds via some intermediate steps and the final residue was not platinum metal alone. Trace amounts of stable compounds (one such possibility might be $[(CH_3)_3PtCl]_4)^{13}$ could be formed in the decomposition and retained in the residue.

While the TG results are indicative of the processes occurring in thermal decomposition, it is the results from the programmed probe thermal analysis which afford us the opportunity for informed speculation on the mechanism of the decompositions. since the evolved species are monitored directly. In fact, it was possible to discern that all complexes, with the exception of Zeise's salt were marginally volatile with parent ions being clearly visible, a result certainly not apparent from the TG experiments.

From Fig. 4 and Table 2 it can be seen that for complexes with L = py, py–NO, 4-CH_3–py and 4-CH_3–py–NO, there are three major losses in which variations in the intensity of the *m/e* = 36 curve (HCl) correspond to the variations in total ion current. When L = $NH(CH_3)_2$, the curves *m/e* = 45 (amine) and *m/e* = 28 (ethylene) indicate that both species are lost simultaneously, while the *m/e* = 36 species is lost independently of all others.

For the complexes in which L = 4-CH_3–py and py, when the peak corresponding to ethylene (*m/e* = 28) was decreasing in intensity, it was observed that peaks of *m/e* values higher than that of the parent were appearing. On the basis of this result, the complexes were pyrolyzed at temperatures corresponding to minima in the *m/e* = 28 curves and the evolved gas identified. The results are given in Table 3.

For each residue resulting from these pyrolyses, the mass spectrum was taken. For the residues from Zeise's salt and the dimethylamine complex, the spectra resembled decomposition spectra in that no high molecular weight species were observed. However, spectra arising from the residue from complexes in which L = py, py–NO, 4-CH_3–py and 4-CH_3–py–NO indicated the presence of species at higher *m/e* values than that of the parent complex. For L = py and py–NO these higher molecular weight species were centered on *m/e* = 423 whilst for L = 4-CH_3–py and 4-CH_3–py–NO they were centered on *m/e* = 451. Also, spectra for the residues of the py and py–NO complexes were identical (Fig. 7), as were those of the 4-CH_3–py and 4-CH_3–py–NO residues.

TABLE 3

L	*Pyrolysis temp.*	*Evolved gases*
py	200	$CH_2=CH_2$
py–NO	200	$CH_2=CH_2$
4-CH_3–py	160	$CH_2=CH_2$
4-CH_3–py–NO	160	$CH_2=CH_2$
$HN(CH_3)_2$	160	$CH_2=CH_2$ + $HN(CH_3)_2$
Zeise's salt	230	$CH_2=CH_2$ + HCl

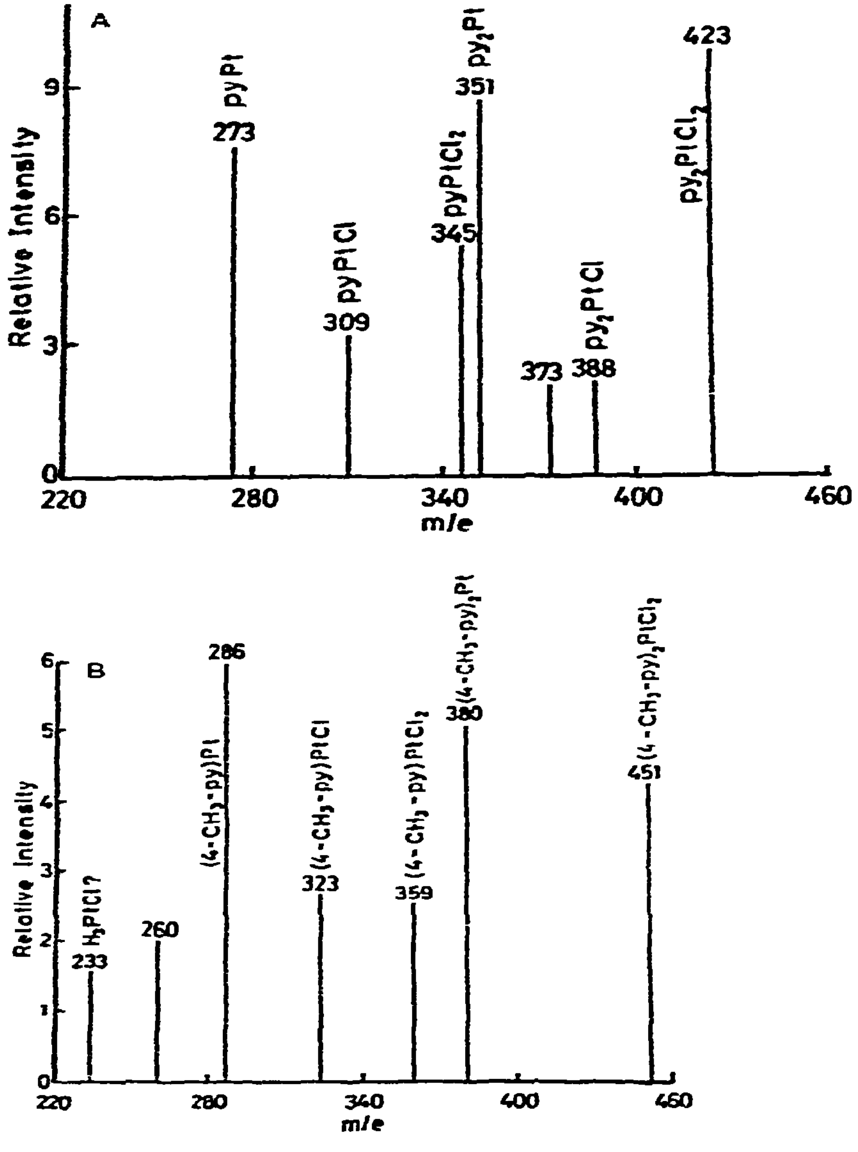

Fig. 7. Monoisotopic mass spectra of the residues from low temperature pyrolyses of $(C_2H_4)^{195}Pt^{35}Cl_2 \cdot L$. A, L = py and py-NO; B, L = 4-CH_3-py and 4-CH_3-py-NO.

These results give a very strong indication of the presence of intermediate species of general formula[14] L_2PtCl_2 (where L = py, py-NO, 4-CH_3-py and 4-CH_3-py-NO), since *m/e* 423 corresponds to $(C_5H_5N)_2\ ^{195}PtCl_2$ and *m/e* = 451 to $(CH_3C_5H_4N)_2\ ^{195}PtCl_2$. Other peaks arising from fragmentation of these parents are shown in Figs. 7A and B. Obviously, in the case of the N-oxide complexes, there is also an oxygen elimination step.

As a result of these observations, it is possible to postulate a decomposition mechanism involving the L_2PtCl_2 species as an intermediate for all the complexes

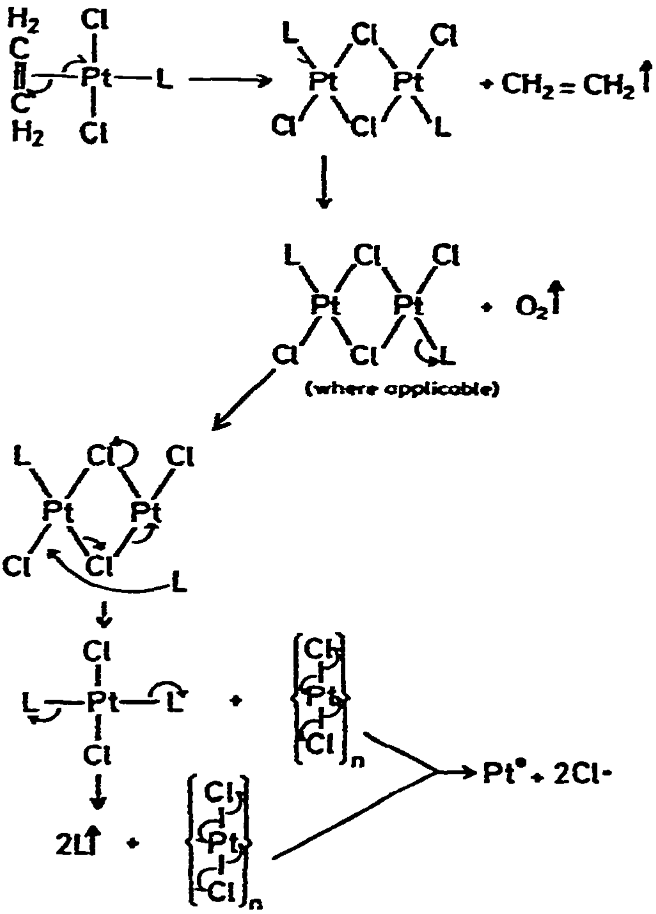

Fig. 8. Proposed decomposition pathway for $(C_2H_4)PtCl_2 \cdot L$, where L = py, py–NO, 4-CH_3–py and 4-CH_3–py–NO. (It seems appropriate to use the symbolism of mass spectrometric fragmentation[17] here.)

involving L = py, py–NO, 4-CH_3–py and 4-CH_3–py–NO (Fig. 8). When L = $HN(CH_3)_2$, however, the situation is similar, but the observation during pyrolysis that the amine and ethylene are evolved simultaneously requires us to superimpose another process, the parent complex decomposing directly to $PtCl_2$ polymer (Fig. 9).

The data we have for Zeise's salt permits only a tentative suggestion that dehydration precedes the ethylene elimination, the resulting anion breaking down to $(PtCl_2)_n$ and KCl. We have no evidence at this stage for a dimeric form of intermediate, although it is interesting to note that Zeise's dimer $[PtCl_2(C_2H_4)]_2$ is reported to form as a step in the thermal decomposition of Zeise's salt[15]. In that paper also, the decomposition of Zeise's dimer was supposed to proceed via

$$[PtCl_2(CH_2CH_2)]_2 \rightarrow Pt + PtCl_2 + Cl_2 + 2(CH_2{=}CH_2)$$

In this work, however, we have found no evidence for the evolution of Cl_2 gas. Whenever chlorine is evolved, it is in the form of HCl. This suggests that chlorine

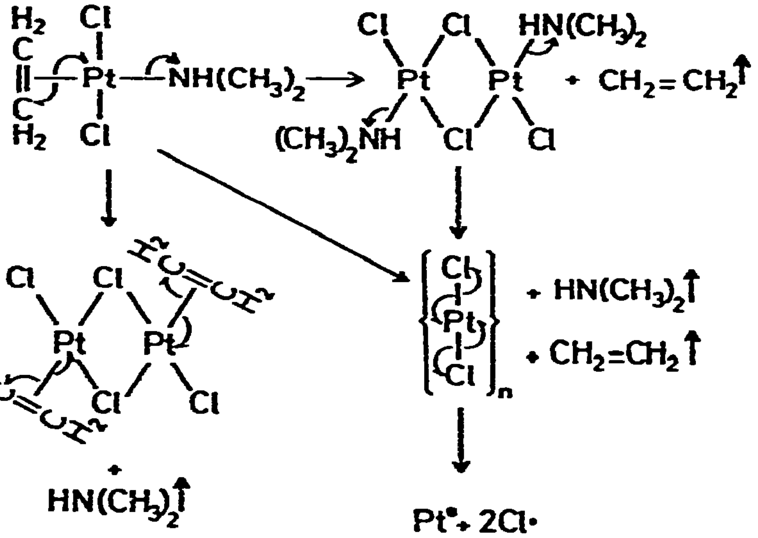

Fig. 9. Proposed decomposition pathway for $(C_2H_4)PtCl_2 \cdot NH(CH_3)_2$. (It seems appropriate to use the symbolism of mass spectrometric fragmentation[17] here.)

breaks off as Cl· and abstracts a hydrogen atom from the surroundings. Such a radical process superimposed on the other processes described, further adds to the complexity of the system.

For programmed probe thermal analysis, a number of difficulties remain. If the sample is volatile at the pressure in the mass spectrometer, decomposition may not be observed. Less volatile samples usually yield mass spectra of the compound, mixed with mass spectra of decomposition products. It is then necessary to be sure that ions observed are not, in fact, fragment ions of the mass spectral fragmentation of the compound, rather than of decomposition products.

A further problem with partially volatile samples is that they may sublime away from the heat source. As the temperature is increased the sublimed material is reheated and results in a smearing of the data.

The problem of volatile samples is being approached by carrying out the decomposition in a small furnace attached to a jet separator normally used as a GC interface. A flow of helium is passed over the sample and then into the interface where the helium is pumped away, leaving the products to pass into the ion source. Preliminary results using this technique show promise[16].

A second problem is that of impurities since ions observed may be the result of decomposition of impurities. However this problem is common to all techniques. Other minor problems are the possibilities of non-uniform heating of the sample and decrepitation. The effects of the latter are alleviated by ensuring that the sample is finely powdered.

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