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SIMULTANEOUS THERMOANALYTICAL INVESTIGATIONS OF $(C_6H_5)_4AsCl$ AND $(C_6H_5)_4PCl$ UNDER AIR AND ARGON ATMOSPHERES

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Abstract

The thermoanalytical curves of $(C_6H_5)_4AsCl$ (I) and $(C_6H_5)_4PCl$ (II) were generated simultaneously by using a Netzsch simultaneous thermal analyser 409 under static air and dynamic argon atmospheres. The ranges of thermal stability of I and II were found to be 145–310°C and 137–365°C, respectively, and their melting points to be 261 and 278°C. The DTA profiles of I and II differ and can be used for their distinction.

Keywords: $(C_6H_5)_4AsCl$ and $(C_6H_5)_4PCl$, TG-DTG-DTA

Introduction

A huge number of tetraphenyl complexes have been prepared and used for industrial, agricultural, medical and analytical purposes. For instance, $(C_6H_5)_4AsCl$ (I) and $(C_6H_5)_4PCl$ (II) have been utilized for the titrimetric determination of Hg [1], for the polarographic determination of Sn [2], for the gravimetric determination of Tc and Re [3], for the determination of Bi and Co [4], and so on. They are well-known precipitants for anions such as permanganate, perrhenate, pertechnate, perchlorate, etc. For stoichiometric analysis, the two precipitants must be dried carefully and their m.p.-s checked frequently; this can easily be performed by thermal analysis. As far as the authors are aware, the thermoanalytical behaviour of I and II has not been investigated. This paper therefore describes such behaviour.

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Experimental

All chemicals used were analytical grade reagents obtained from Fluka AG (Buchs). Samples were carefully ground for 20 minutes with an agate mortar and pestle. Solid degradation products were identified with a Philips 1140 X-ray diffractometer.

All thermoanalytical curves were generated with a Netzsch simultaneous thermal analyser 409. Other instrumental parameters have been discussed elsewhere [5]. For brevity, not all DTG curves are shown in Figs 1–4.

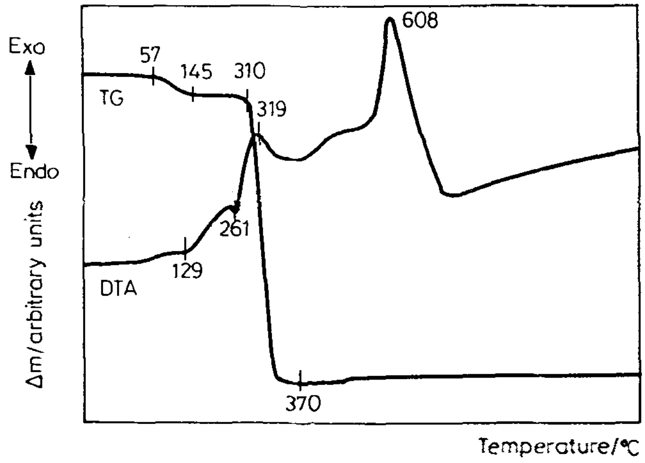

Fig. 1 $(C_6H_5)_4AsCl$ under air atmosphere

Results and discussion

Thermal behaviour of I

The DTA curve in Fig. 1 shows that with increasing temperature the mechanically bound water begins to be lost at about 57°C. This relatively very slow process takes place at a maximal rate at about 129°C. The water lost amounts to 3.16 wt%. Between 145 and 310°C, dry I is thermally stable. This range of temperature should be recommended for the quantitative drying of I. A small sharp endo-peak with ΔT_{min} = 261°C describes the m.p. of I (literature value = 256–259°C). Thereafter (> 310°C), simultaneous oxidation, volatilization and degradation of the sample occurs, resulting in a weight loss of 40.62 wt%, calculated on a dry basis.

The exotherm (ΔT_{max} = 319°C) does not suggest a stepwise mechanism and therefore the spontaneity of the sudden process is clear. The released $AsCl_5$ (detected by chemical analysis of evolved pyrolysates) escapes since it is volatile at high temperature (310°C), whereas the organic part of I (i.e. the phenyl groups) are oxidized and burned, with final conversion into water vapour and carbon. X-ray diffractometry of the end-product of the thermal degradation confirmed the presence of graphite. No explanation could be offered for the inhibition of graphite air oxidation over the range 400–1000°C (the ceiling temperature of the heating program). The shape of the DTA curve above 400°C can probably be explained by a change in thermal conductivity or heat capacity, but not, as was thought earlier, the transformation coal → graphite, since the change in enthalpy of this process would be too large.

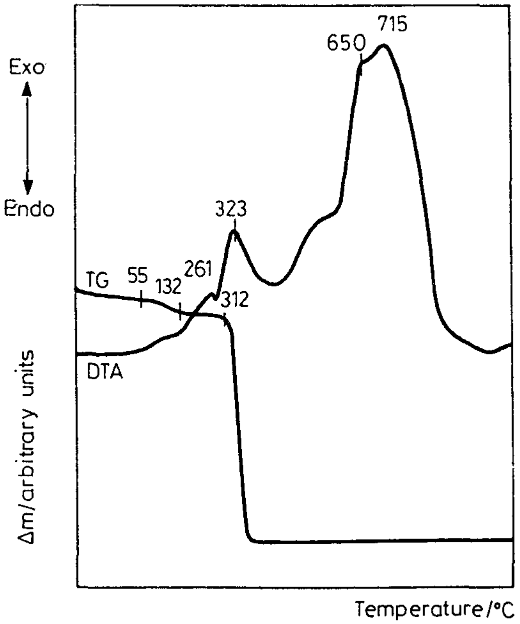

Fig. 2 $(C_6H_5)_4AsCl$ under argon atmosphere

In argon (Fig. 2), a mode of thermal behaviour very similar to that in air is exhibited by I except that the range of thermal stability is a little wider (132–312°C). However, the rate of change in heat capacity is lower, as seen from the broad hump in the vicinity of 650–715°C.

Thermal behaviour of II

Figure 3 depicts the thermal curves of II in an air atmosphere. The first and second decomposition periods of the TG curve extending up to 137°C reflect the escape of the mechanically bound water, with a weight loss of 2.32 wt%. Between 137 and 365°C, a very slow decrease in weight takes place. The small sharp endotherm (ΔT_{min} = 278°C) represents the m.p. of II (literature

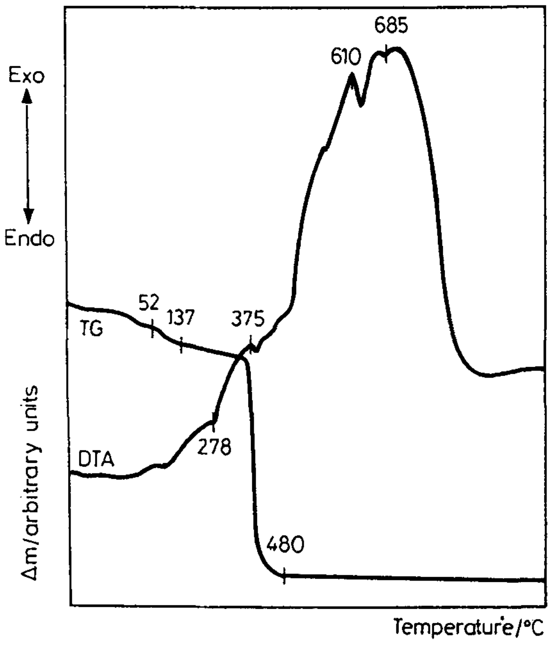

Fig. 3 $(C_6H_5)_4PCl$ under air atmosphere

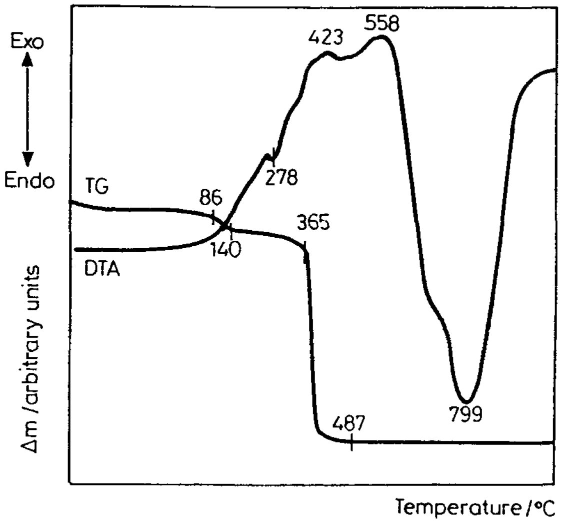

Fig. 4 $(C_6H_5)_4PCl$ under argon atmosphere

value = 275–280°C). Simultaneously with the decomposition of II, the DTA curve indicates a small exothermic process (ΔT_{max} = 375°C), corresponding to the oxidation, degradation and combustion of the organic part of II, i.e. the phenyl groups, and also the escape of PCl_5. The weight loss computed on a dry basis was found to be 43.80 wt%. The exotherm with maximum at 610°C describes the change in the heat capacity. The endotherm at 685°C can probably be attributed to a crystalline phase change (rhombic) of graphite.

Figure 4 shows the thermal curves of II in argon atmosphere. The decomposition process can be divided into two main periods: up to 140°C, humidity and mechanically bound water is lost. At 140–360°C, a very slow decrease in weight of the dried sample is observed, which suggests the absence of a definite horizontal plateau suitable for the stoichiometric drying to II. In this connection, I could be regarded as a better precipitant than II. The exotherm which accompanies the degradation of II in air is not observed in argon because of the oxygen deficiency. Incidentally, it is likely that O_2 plays the role of both oxidizer and catalyst at high temperatures. Phosphorus species could not be detected in the end-products. The prominent difference in shape of the profiles of the DTA curves of II in the two atmospheres indicates that there must be a disproportion between the mechanisms of decomposition in the two atmospheres.

References

1 F. Junge, Z. Anal. Chem. Fresenius, 173 (1960) 243.
2 Merck Index 11, 9167.
3 F. Jasim, R. J. Magee and C. L. Wilson, Talanta, 4 (1960) 17.
4 Beil. 16, IV, 984–985.
5 F. Jasim and S. A. Ali, J. Thermal Anal., in press.
6 F. Jasim, A Textbook of Thermal Analysis, Baghdad University Press, Baghdad, 1985 (in Arabic).

Zusammenfassung — Mit Hilfe eines Netzsch 490 Thermoanalysegerätes wurden in statischer Luft und in dynamischer Argonatmosphäre simultan die thermoanalytischen Kurven von $(C_6H_5)_4AsCl$ (I) und $(C_6H_5)_4PCl$ (II) aufgenommen. Die thermische Stabilität der Verbindungen I und II liegt im Bereich 145–310°C bzw. 137–365°C, ihre Schmelzpunkte betragen 261 bzw. 278°C. Der DTA-Kurvenverlauf von I und II ist unterschiedlich und kann zu ihrer Unterscheidung verwendet werden.