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INVESTIGATION OF THE DECOMPOSITION PRODUCTS OF SEVERAL ORGANOMETALLIC COMPOUNDS BY PYROLYSIS GAS CHROMATOGRAPHY

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The application of Curie-point pyrolysis followed by gas chromatographic analysis of the reaction products in thermal decomposition studies on several organometallic compounds containing σ-alkyl and cyclopentadienyl ligands is presented.

One of the methods suitable for the study of thermal decomposition and the decomposition products of different solid samples is flash pyrolysis followed by gas chromatographic analysis of the reaction products [1]. The application of this method to organometallic compounds has recently been mentioned [2, 3]. We now wish to report the application of this method for thermal decomposition studies on several alkylplatinum compounds and cyclopentadienyl complexes of iron, nickel and platinum.

Preparation of samples

Iodotrimethylplatinum(IV) was prepared by the method of Clegg and Hall [4]. Chlorotrimethylplatinum(IV) was prepared by adding an aqueous solution of potassium chloride to an aqueous solution of trimethylplatinum(IV) sulphate [5]. Bromotrimethylplatinum(IV) was prepared in a similar manner to the chloro compound, but using KBr [6]. The purities of the trimethylplatinum(IV) halides were checked via their near and far IR spectra.

Ferrocene was purchased from Ventron Corp. Nickelocene was prepared using a standard procedure [7].

The advantage of the applied method is: (i) good qualitative and quantitative determination of decomposition products, (ii) short reaction time, (iii) very small sample size. This latter is very important in organometallic chemistry where the amount of compound available is often very limited. Solid samples of the complexes as fine powder were placed on the Curie-point wire. Attempts to coat the wire from concentrated solutions of these complexes were unsuccessful. To avoid loss of the powder coated onto the Curie-point wire, the end of the wire was fined away to form a foil shape and the sample was placed in the V shape of the foil. With this procedure, good reproducibility was achieved in the 100—600 μg sample range.

In our series of experiments a Packard 891 Curie-point Analyser and Packard gas chromatograph with FID and TC detectors working simultaneously were used. 1/8 inch O. D. glass columns packed with Poropak Q or Chromosorb AW-DMCS coated with 10% Apiezon L were applied.

Table 1

Pyrolysis of $[(CH_3)_3PtCl]_4$; change of C_2H_6/C_2H_4 ratio with pyrolysis time

Pyrolysis time, sec	Temperature of pyrolysis, °C	
	358 C_2H_6/C_2H_4 ratio	480 C_2H_6/C_2H_4 ratio
0.5	13.6	—
1.0	6.5	2.1
2.0	2.5	1.4
4.0	0.9	0.6
6.0	0.6	—

Sample weight: 300 μg

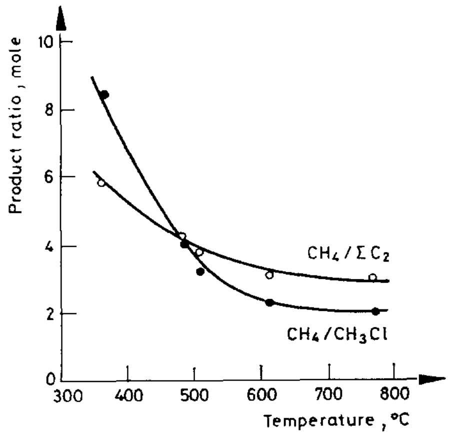

Fig. 1. Product ratio *vs.* temperature curves. Cluster: $[(CH_3)_3PtCl]_4$, sample weight: 300 μg, Pyrolysis time: 1 sec

Together with the expected thermal decomposition products of $[(CH_3)_3PtX]_4$ (where $X = Cl, Br, I$), such as methane, ethane ethylene and methyl halides, hydrogen cyclopropane and propylene were also detected. Significant differences in product distribution were observed at different temperatures (358, 480, 510, 610 and 770°), different pyrolysis times (1, 2, 4, 6 sec) and on the change of group X

in $[(CH_3)_3PtX]_4$. In Fig. 1 the relationship between the ratio of the main decomposition products of $[(CH_3)_3PtCl]_4$ and the pyrolysis temperature is illustrated. At lower temperatures the decomposition is directed towards methane formation. On the basis of the smaller amount of CH_3Cl formed at 358°, an alternative route of chlorine elimination could be suggested. In our TG-MS studies [4] the formation of hydrogen halides was demonstrated. This reaction route is probably responsible for the high CH_4/CH_3Cl ratio at 358°. The considerable change of the C_2H_6/C_2H_4 ratio with the pyrolysis time, as shown in Table 1, suggests that a secondary reaction is involved in ethylene formation. The higher amount of hydrogen obtained on longer pyrolysis also indicates that part of the ethylene may have been formed in ethane dehydrogenation catalyzed by platinum metal formed.

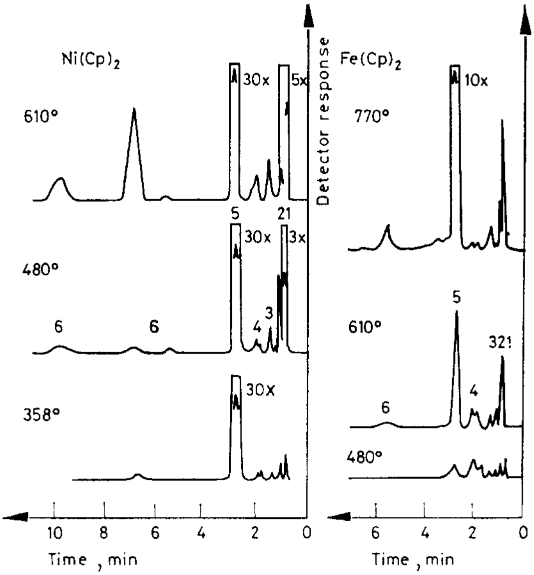

Fig. 2. Pyrograms of Cp_2Fe and Cp_2Ni at different temperatures. Pyrolysis time: 1 sec. GC conditions: column: 10% Apiezon L on Chromosorb AW-DMCS, length: 7 f_t; carrier gas: nitrogen, flow rate: 35 ml/min, Column temperature: 70°C. 1 — CH_4, C_2H_4, C_2H_6; 2 — C_3 hydrocarbons; 3 — C_5 hydrocarbons; 3 — C_5 hydrocarbons; 5 — cyclopentadiene; 6 — unkown

More complicated product formation was obtained for bis-cyclopentadiene (Cp) complexes of Fe and Ni. The large variety of decomposition products is due to the fragmentation of the cyclopentadienyl ring. Among the decomposition products are methane, ethane, ethylene, and C_3, C_4 and C_5 hydrocarbons. The main product of pyrolysis is cyclopentadiene. For a more detailed characterization of the reaction products, further GC-MS analysis is necessary.

In Fig. 2 pyrograms (fingerprints) are shown for Cp_2Fe and Cp_2Ni at different temperatures. In the short-time pyrolysis experiments evaluable differences in the thermal stability and in the thermal decomposition route were obtained for these two bis-cyclopentadienyl complexes. A considerable decomposition of ferrocene takes place only at 770°, whereas nickelocene decomposes readily at 358°. There is also a significant difference in the reaction products distribution, which may indicate different decomposition routes for these types of complexes.

For $(CH_3)_3PtCp$ the main product of decomposition is methane. Ethane was formed in smaller quantities, and only traces of hydrogen and ethylene were detected. The lack of C_3 and C_4 hydrocarbons indicates the relatively high stability of the cyclopentadienyl ring against fragmentation. The ratios of the decomposition products at 358 and 480° are shown in Table 2. On the basis of the high CH_4/C_5H_6 ratio, one can suggest that the dehydrogenation of the C_5H_5 ring is involved in the formation of methane, i.e. the cyclopentadienyl ring can be considered as a hydrogen source. The high carbon content of the decomposition product supports this suggestion.

Table 2

Pyrolysis of $(CH_3)_3PtCp$

Product ratio (molar)	Temperature of pyrolysis, °C	
	358	480
$\frac{CH_4}{C_2H_6}$	14.6	19.2
$\frac{CH_4}{C_5H_5}$	4.5	5.0

Pyrolysis time: 2 sec; sample weight: 120 μg

Our current studies are focused on acquiring more detailed results on the decompositions of alkyl derivatives of platinum and different bis-cyclopentadienyl complexes.

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RÉSUMÉ — La décomposition thermique de plusieurs composés organométalliques contenant des ligands σ-alcoyliques et cyclopentadiényliques a été étudiée en appliquant la technique de la pyrolyse au point de Curie, suivie par analyse chromatographique en phase gazeuse des produits de réaction.

ZUSAMMENFASSUNG — Der Einsatz der Curie-Punkt Pyrolyse mit nachfolgender gaschromatographischer Analyse der Reaktionsprodukte zur Untersuchung der thermischen Zersetzung verschiedener metallorganischer Verbindungen mit σ-Alkyl- und Cyclopentadienylliganden wird beschrieben.

Резюме — Представлено применение пиролиза при точке Кюри с последующим газовым хроматографическим анализом продуктов термического разложения некоторых металлоорганических соединений, содержащих σ-алкильный и циклопентадиенильный лиганды.