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## SHORT COMMUNICATION

### New Syntheses of Platinum (IV) and Platinum (VI) Fluorides

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The first method used to prepare platinum hexafluoride was to burn a platinum wire in a fluorine atmosphere adjacent to a surface cooled by liquid nitrogen [1,2]. The platinum wire was electrically heated to initiate the reaction. Even with this special technique, some lower platinum fluorides were formed and the yield of platinum hexafluoride was about 70 %. Platinum hexafluoride was also prepared from a platinum sponge and elemental fluorine under pressure at 500°C [3]. The yield of this reaction was not reproducible but varied from 10% up to even 90 % in some cases.

It has now been determined that 200°C is a very convenient reaction temperature for the pressure synthesis of platinum hexafluoride. According to Weinstock et al. [2], the rate of thermal decomposition of platinum hexafluoride in the presence of fluorine at high pressure is significant only above 200°C, while the reaction rate for the formation of platinum hexafluoride is still high enough at 200°C, although the formation of platinum hexafluoride is more favorable at higher temperatures [2].

In a typical experiment, the platinum sponge (0.8 g) was weighed into the reaction vessel (100 ml) and thoroughly dried in a dynamic vacuum. Elemental fluorine was then metered into the reaction vessel (15 atm as measured at 22°C with the mole ratio  $\text{Pt}:\text{F}_2 = 1:15$ ). The reaction was carried out at 200°C for several hours, after which the reaction vessel was cooled down and excess fluorine was pumped away. The yield of platinum hexafluoride was only 40 to 50 % as was shown by the difference in weight before and after pumping away all the platinum hexafluoride. The remainder was lower platinum fluorides ( $\text{PtF}_x$  with  $x$  being between 4 and 5) as was estimated from the mass balance of fluorine which was followed throughout the experiment with an accuracy of  $\pm 1$  mg. Better yield of platinum hexafluoride was obtained by using a reaction vessel equipped with a finger in the upper part cooled by liquid nitrogen. In this case the yield of platinum hexafluoride was 70 to 75 %. The remainder was again lower platinum fluorides. Additional fluorination was inefficient with regard to higher yield of platinum hexafluoride. The purity of the sample was checked by chemical analysis (Calcd. for  $\text{PtF}_6$ : F = 36.88; Pt = 63.12, Found: F = 36,5; Pt = 62,8).

Platinum tetrafluoride is usually prepared by thermal decomposition of the 2:1 bromine trifluoride–platinum tetrafluoride adduct under vacuum at 180°C [4]. However, Bartlett et al. found that platinum tetrafluoride obtained in this manner is always contaminated with bromine which, however, could be completely removed as bromine pentafluoride by fluorinating with diluted fluorine at 250°C [5]. We have now found that thermal decomposition of platinum hexafluoride is a useful method for the preparation of pure platinum tetrafluoride.

In a typical experiment, platinum hexafluoride and lower platinum fluorides which were obtained as described above, were thermostated at 200°C for several hours. Then elemental fluorine was pumped away, and thermal decomposition was repeated two or three times. The end product was platinum tetrafluoride as shown by mass balance, X-ray powder diffraction photographs, magnetic susceptibility measurements, and infrared spectroscopy. The purity of the sample was checked by chemical analysis (Calcd. for PtF<sub>4</sub>: F = 28.04; Found: F = 28.1 %).

The advantages of our new syntheses are that they are simple and fast, with reasonably high yields. The products obtained are pure.

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- 3 J. Slivnik, A. Šmalc and A. Zemljič, 3<sup>rd</sup> International Symposium on Fluorine Chemistry, München, 1965.
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#### Erratum

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**Journal of Fluorine Chemistry, Vol. 15 No. 2, Contents list.**

The paper on Polycyclic fluoro-aromatic compounds by J. Burdon, I. W. Parsons and H. S. Gill, has unfortunately been given the wrong subtitle:

Part III. Syntheses..... and derived  
should read:

Part VIII. The preparation of perfluorochrysene and some related compounds.