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Simultaneous fluorination and oxidation of iridium by metal tetrafluorobromates

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Abstract

Iridium is one of the most important platinum group metals and is used in several alloys and in the automotive industry for the purposes of making catalysts. Therefore, its recycling is a very actual challenge for researchers working in the field of urban mining. Reactions of various tetrafluorobromates $M\text{BrF}_4$ ($M = \text{K}, \text{Rb}, \text{Cs}$) and $M'(\text{BrF}_4)_2$ ($M' = \text{Ba}$) with Ir metal have been investigated. Compositions of the obtained products have been determined, corresponding reaction schemes have been suggested, and proper conditions for the reactions have been established.

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1. Introduction

Scientific as well as industrial interest in extraction and separation of valuable components from municipal solid wastes, the so called “urban mining”^{1,2,3} is steadily growing. Such components contain such expensive rare metals as e.g. indium, the noble, or rare earth metals. These metals are usually used in different parts of electronic devices, supplies, or catalysts in quite small amounts. Although a lot of investigations in order to develop a process to re-obtain these resources have been carried out, a universal solution has not yet been found³.

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Simultaneous treatment of all noble metal compounds in urban solid wastes to convert them into complex fluorides may present such a universal solution. In comparison to traditional techniques for the homogenization of materials (e.g. grinding and dissolving in aqua regia or nitric acid), this method is more convenient mainly due to the fact that there are no liquid wastes formed at the first stage of the process. However, the question of choosing an effective and convenient fluorinating agent arises in this case. The most obvious choice – elemental fluorine – not always appropriate, since technologies involving fluorine require special safety measures for its storage and transportation. Also it is due to the necessity of higher temperatures in several reactions with noble metals. As far as simple fluorination is concerned, hydrogen fluoride, hydrofluoric acid, ammonium fluoride, and other fluorinating agents can be used for application. But if the fluorinating process is supposed to be oxidative at the same time, i.e. not only fluorides of different elements must be obtained but also their simultaneous oxidation is to be achieved, then metal fluorides in their highest oxidation states, noble gas fluorides, or halogen fluorides can be used as oxidizers. Halogen fluorides (BrF_3 , ClF_3 , etc.) are used in several branches of industry^{4,5}, however, their application is even more complicated when it comes to the safety and staff qualification requirements.

It may also be possible to use the relatively uninvestigated substance class of alkali and alkaline-earth tetrafluorobromates^{6,7,8,9,10} for the extraction and successive separation of noble metals. The oxidative fluorination of iridium metal is studied in this article, since this element has especial importance in the context of urban mining: In industry, iridium is used as a hardening agent in alloys for the purposes of making metallurgical instruments and electrical contacts. Moreover, iridium is the most recent platinum group element to be used in new-generation catalytic converters for the reduction of nitrogen oxides emission in the motor industry¹¹. This makes the recycling of Ir a high priority challenge in the present day context.

The compounds, which form the substance class of tetrafluorobromates, are corresponding Lewis acids and bases (bromine trifluoride and metal fluorides). Tetrafluorobromates have a number of advantages in comparison to many other fluorinating agents: Under ambient conditions the tetrafluorobromates are the solid substances which have a low equilibrium pressure of bromine trifluoride and are stable in dry air. All tetrafluorobromates exhibit their fluorinating and oxidative properties only when being thermally decomposed. This fact significantly simplifies all processes with their usage, such as handling, storage, and transportation¹².

In this study, we present the results of the X-ray powder diffraction analyses of the products formed in the reactions of various tetrafluorobromates with iridium metal.

2. Results and discussion

Since the alkali metal tetrafluorobromates show oxidative properties during melting and/or decomposition, the first stage of our investigation was to obtain the proper reaction conditions in favor of a high yield of oxidized iridium compounds. The chosen conditions and the technological description of the experiments are given in the *Experimental* section.

In order to determine a general composition of the formed products, an interaction of iridium metal with a large excess of potassium tetrafluorobromate $\text{Ir}:\text{KBrF}_4=1:12$ (mass) / 1:11.8 (molar) has been carried out. The formed products have been identified with the help of the X-ray powder diffraction analysis. A typical diffraction pattern is shown in Fig. 1.

Comparisons of the diffraction patterns with the ones from the international diffraction database PDF-2¹³ showed that the interaction products mainly consisted of two phases: potassium hexafluoroiridate (IV) K_2IrF_6 and some unreacted excess of potassium tetrafluorobromate KBrF_4 . The other crystalline phase(s) present could not be identified. CIF-files of these substances have been taken from the crystallographic database ICSD¹⁴ (cards #95779 and #10326, respectively). The obtained powder pattern has been refined using the Le Bail algorithm¹⁵, the results of profile fitting are shown in the caption of Fig. 1. The calculated ratio of the products has been obtained from the subsequent Rietveld refinement¹⁶ and has been approximately equal to $\text{K}_2\text{IrF}_6:\text{KBrF}_4=1:12$ (mass) / 1:24 (molar). The following reaction scheme 1 is suggested to describe the process:



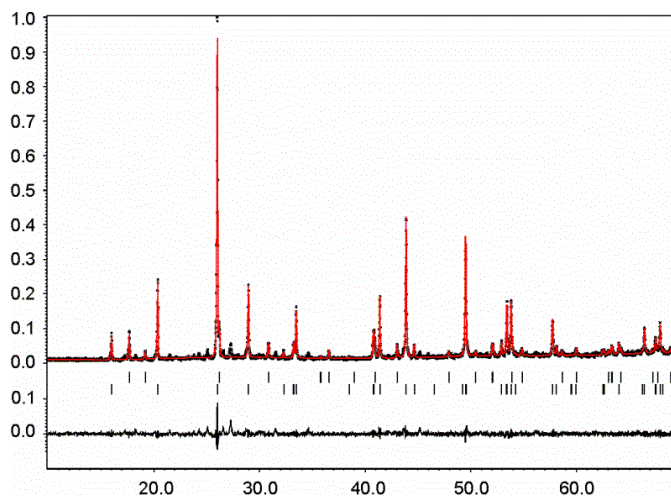


Fig. 1. Powder diffraction pattern of the products of the Ir:KBrF₄ = 1:12 (mass) / 1:11.8 (molar) reaction. Experimental data (black crosses), calculated powder profile (red), and difference profile (bottom, black). The calculated reflection positions are shown as black ticks (K₂IrF₆ – first row, KBrF₄ – second row). $R_p = 0.1047$, $R_{wp} = 0.1487$.

Although the product ratio (1:12 by mass) obtained using the Rietveld algorithm differs from the calculated (1:5 by its mass) ratio derived from the equation 1, the suggested scheme should be plausible because KBrF₄ and K₂IrF₆ are the major products present in the powder pattern (Fig. 1).

The interaction of stoichiometric amounts (according to the equation above) of iridium metal and potassium tetrafluorobromate has also been investigated. A typical corresponding powder diffraction pattern together with le Bail refinement is shown in Fig. 2. The reaction of the stoichiometric mixture was supposed to yield phase-pure potassium hexafluoroiridate(IV). However, the results of the powder X-ray diffraction analysis indicated again the presence of some unreacted potassium tetrafluorobromate in the product mixture with the calculated KBrF₄:K₂IrF₆ = 1:4.9 (mass) / 1:2.5 (molar) ratio. Perhaps this can be explained by the thermodynamic equilibrium that is likely to exist between reactants and products because the reaction was carried out inside a closed container.

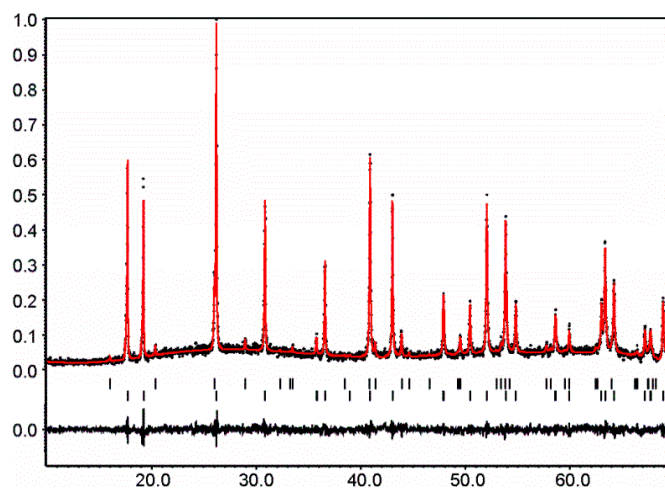


Fig. 2. Powder diffraction pattern of the products of the Ir:KBrF₄ = 1:2.03 (mass) / 1:2 (molar) reaction. Experimental data (black crosses), calculated powder profile (red), and difference profile (bottom, black). The calculated reflection positions are shown as black ticks (KBrF₄ – first row, K₂IrF₆ – second row). $R_p = 0.0884$, $R_{wp} = 0.1230$.

If an under-stoichiometric amount of KBrF_4 is used ($\text{Ir}:\text{KBrF}_4=1:1$ by its mass, 1:1.02 by moles), the product mixture shows reflections corresponding to potassium hexafluoroiridate (IV) K_2IrF_6 and iridium metal with the calculated $\text{Ir}:\text{K}_2\text{IrF}_6 = 1:9.3$ (mass) / 1:4.7 (molar) ratio. The obtained powder X-ray diffraction pattern is shown in Fig. 3. Also, a number of reflections that belong to one or several unidentified compounds can be noticed in this pattern. However, they could not be assigned to other known compounds.

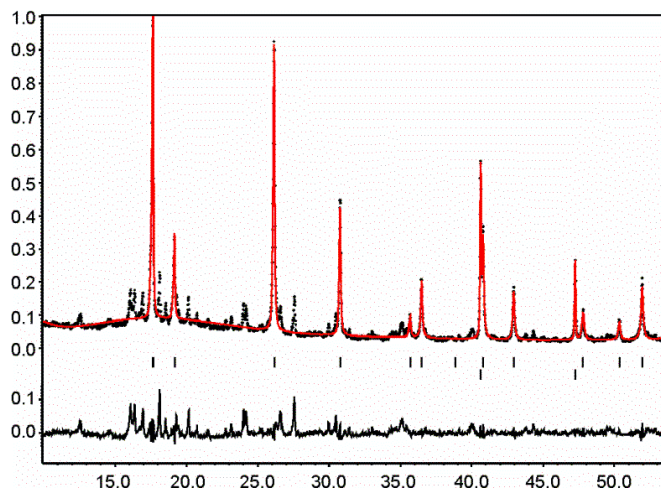


Fig. 3. Powder diffraction pattern of the products of the $\text{Ir}:\text{KBrF}_4 = 1:1$ (mass) / 1:1.02 (molar) reaction. Experimental data (black crosses), calculated powder profile (red), and difference profile (bottom, black). The calculated reflection positions are shown as black ticks (K_2IrF_6 – first row, Ir – second row). $R_p = 0.1149$, $R_{wp} = 0.1644$.

In order to determine the principal possibility of the interaction of iridium metal with other tetrafluorobromates, namely RbBrF_4 , CsBrF_4 and $\text{Ba}(\text{BrF}_4)_2$, a series of experiments with stoichiometric ratios of components has been carried out according to the following chemical equations 2 to 4:



In all cases the formation of the corresponding hexafluoroiridate (IV) has been confirmed. In case of the tetrafluorobromates of barium and cesium no reflections of other phases have been observed. In the reactions of rubidium tetrafluorobromate reflections belonging to an unknown phase have been observed. At this moment, no clear explanation for the nature of these reflections and the composition of the respective compound can be given. Despite the fact that the number of these respective peaks is very limited, we were able to index the cell in the hexagonal crystal system with cell parameters $a = 7.642$, $c = 7.703$ Å, and $V = 389.5$ Å³.

In order to determine the nature of this phase, we have compared it to powder diffraction patterns of K_2IrF_6 and KIrF_6 (in fact, K_2PtF_6 ¹⁷ and KPtF_6 ¹⁸ have been used for comparison, as they were available in the PDF-2 database; the respective cell parameters are similar and the compounds are isotypic). It has been noticed that the relations between peak positions in K_2IrF_6 and KIrF_6 diffraction patterns were the same as in the products of the RbBrF_4 and iridium metal reaction. This may indicate that the second phase in the product is rubidium hexafluoroiridate(V) RbIrF_6 , but further investigation is required. The calculated reflection positions of this phase with the obtained cell parameters are shown in Fig. 4.

3. Conclusion

In this article we have investigated the reactions of tetrafluorobromates with Ir metal. Iridium metal may be converted this way to an easily soluble form¹⁹ for further recovery of the metal. Compositions of the obtained products have been determined, corresponding reaction schemes have been suggested, and further investigations have been established.

The proposed method may be used as a base for the development of a transformation technique of noble metals to soluble forms in order to extract them from solid urban wastes. As far as the problem of separation of the different noble metals that are contained in solid wastes is concerned, similar investigations need to be carried out for each metal in question. This research will be conducted by the authors in the near future.

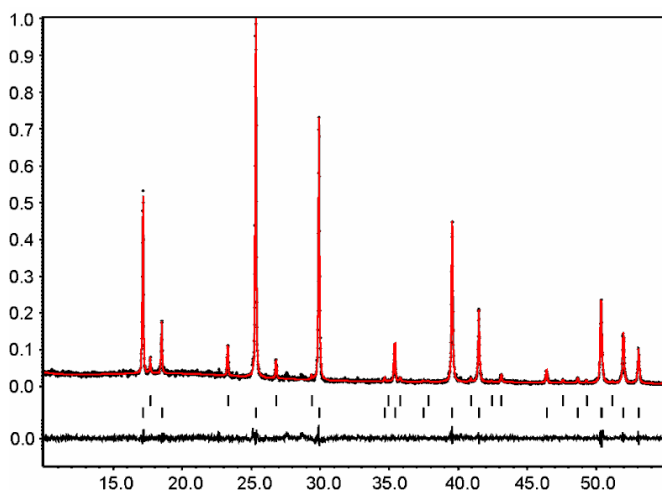


Fig. 4. Powder diffraction pattern of the products of the rubidium tetrafluorobromate with iridium metal reaction in the stoichiometric ratio. Experimental data (black crosses), calculated powder profile (red), and difference profile (bottom, black). The calculated reflection positions are shown as black ticks (unknown phase – first row, Rb_2IrF_6 – second row). $R_p = 0.0795$, $R_{wp} = 0.1109$.

4. Experimental section

All operations have been carried out in an atmosphere of dry and purified argon (WestfalenAG, Germany) in a sealed glove box (MBraun, Germany), so that a possible contact of the substances with moisture or air was minimized ($\text{O}_2 < 1$ ppm, $\text{H}_2\text{O} < 1$ ppm).

Iridium metal has been used as commercially available in the powder form without its further purification or treatment. KBrF_4 , RbBrF_4 , CsBrF_4 , and $\text{Ba}(\text{BrF}_4)_2$ have been synthesized by the bromine trifluoride reaction which had been distilled directly before the synthesis and the respective metal halides (KF , RbCl , CsCl , BaF_2). In-depth description of this technique can be found in the literature^{12,21}.

The reaction of iridium metal with tetrafluorobromates has been carried out in nickel ampoules sealed by arc welding. The ampoules have been previously passivated with fluorine. Before being loaded in ampoules, the mixture of reactants has been pressed into pellets in order to improve their contact surface. The ampoules have been heated in a muffle furnace up to 400 °C for 120 minutes. They were kept for 150 minutes at this temperature and then were slowly cooled down for 240 minutes to room temperature.

Powder X-ray diffraction patterns have been obtained on a Stadi-P-Diffractometer (Stoe, Germany) using $\text{Cu}_{\text{K}\alpha}$ -radiation, a germanium monochromator and a Mythen1K detector. Le Bail profile fitting and the Rietveld refinement has been executed in Jana2006 software²².

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