Research paper

Oxidative fluorination of iridium metal for urban mining: Kinetic studies

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Abstract

The process of oxidative fluorination of a compact iridium metal has been studied. For this purpose, tetrafluoridobromates(III) of alkali and alkaline-earth metals were chosen as oxidizing agents with numerous advantages. The main results of this work include the kinetic dependencies for the two following processes: 1) interaction of iridium with molten potassium tetrafluoridobromate; and 2) interaction of iridium with a solution of potassium tetrafluoridobromate in liquid bromine trifluoride. In both cases it has been found out that iridium can be transformed into its soluble fluorinated derivative; the reaction with molten potassium tetrafluoridobromate proceeds almost 50 times faster (in comparison to the interaction in BrF_3 solution) and can be potentially applied for the practical purposes.
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Keywords: Iridium; Urban mining; Oxidative fluorination; Tetrafluoridobromates; Kinetics

1. Introduction

In a general case, "urban mining" is a complex process of extraction and separation of valuable components (such as precious, rare, and rare-earth metals) from industrial and/or solid urban wastes: used electronics, batteries, magnets, and catalysts. Search for effective methods of recovery of such expensive components as noble, rare, and rare earth metals is a top priority task for modern industry. This fact can be figured out from the recent trends in patent and innovation activities on waste processing, recycling and recovery of materials from consumer products, which grow rapidly in such countries as India, USA, Germany, Japan, etc. [1,2]. Re-obtaining the valuable metals from electronic scrap is extremely important for both economic and environmental reasons, e.g. it improves resource efficiency of production, decreases expenses for raw materials and prevents environmental and health issues of inappropriate landfilling in open dumps [2–5].

Nowadays, numerous technologies for the extraction of a wide range of metals exist [6]. However, an optimal solution has not yet been found because of technological and organization issues. As suggested in Ref. [3], the main challenge in waste processing is to deal with the impurities that are present in waste along with the target metals. Common technologies imply homogenization of an initial scrap material, separation or/and chemical treatment with acids (e.g. hydrofluoric acid or aqua regia). These agents have technological disadvantages such as big amounts of liquid acidic waste formed during the first stage of treatment and long duration of the process. As far as the organization aspects are concerned, the level of recycling of rare, rare earth and noble metals is very limited, and there are only a few companies in Europe that are actively involved in recovery processes while the major part of them deal only with the initial collection, dismantling and pre-processing of scrap [3,7].

In the present work we focused on such prospective oxidizing agents as tetrafluoridobromates(III) of alkali and alkaline-earth metals. This is a substance class with a general formula of $MBrF_4$ (where M = Na, K, Rb, Cs) or $M(BrF_4)_2$, where M = Ba [8–10]. As reported previously in Ref. [11], they demonstrate significant advantages when compared to the above-mentioned traditional techniques, both groups being strong fluorinating agents. This is primarily because these substances are solid and relatively stable under normal conditions. It was previously shown that their extreme oxidative and fluorinating capacity

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reveals during their thermal decomposition [11]. These two facts provide a basis for their convenient usage in such important procedures as decomposition of the most inert samples and treatment of individual noble metals with further conversion into a liquid form and their recovery as solid metals and/or alloys. Numerous experiments were done to confirm successful oxidative activity of tetrafluoridobromates in case of noble metals where a complete transformation into soluble forms was achieved without significant losses [12,13].

In our previous work [11] the detailed studies on oxidative fluorination have involved a series of interactions of iridium metal with potassium tetrafluoridobromate in different ratios: a high excess of fluorinating agent with Ir:KBrF$_4$ = 1:12 by mass/1:11.8 (molar), as well as in stoichiometric, and understoichiometric ratios (Ir:KBrF$_4$ = 1:1 by mass, 1:1.02 by moles) in terms of the following reaction:

$$Ir + 2\,KBrF_4 = K_2IrF_6 + 2\,BrF \qquad (1)$$
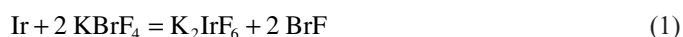
The experiments on interactions between iridium and tetrafluoridobromates of Rb, Cs, and Ba in stoichiometric ratios were also carried out [11]. All the principal results including the phase analysis by means of X-ray powder diffraction as well as simultaneous thermogravimetric and differential thermal analyses of reaction mixtures were obtained and interpreted. In summary, it was shown that in all cases it was possible to obtain the corresponding hexafluoridoiridates(IV).

However, for the practical application in analytical chemistry and industry, a deeper insight into the above-mentioned oxidative fluorination process is crucial. In the present work we report the results of our detailed investigations on the kinetics of the oxidative fluorination of iridium metal. Iridium has been chosen for the study because this metal has special importance for industry. It is commonly used as a hardening agent in thermo-resistive alloys and as a component of several catalysts in oil refinery and in automobile industry for reduction of nitrogen oxide emissions. In a compact form, this metal exhibits strong chemical resistance to aggressive media of organic and mineral acids that significantly complicates its transformation into a soluble form for further recovery [13].

2. Materials and methods

For the described kinetic studies, BrF$_3$ was used as a solvent for KBrF$_4$ in the temperature range up to 130 °C (403 K, close to the boiling point of pure BrF$_3$). At the temperature of 400 °C (673 K) pure KBrF$_4$ was used as a fluorinating agent.

All experiments were carried out in isothermal conditions; the temperature measurements were recorded using a chrome–aluminum thermocouple and the device for data acquisition "cFP–2100" (National Instruments). The accuracy of temperature control was ±0.25 K. Iridium metal was used in a form of small cylinders with the diameter of 2.5 mm and the length exceeding the diameter no more than 1.8 times, with a total mass of ~0.5 g and purity of 99.9%.

2.1. Synthesis of BrF$_3$

Bromine trifluoride was synthesized in a nickel reactor using liquid bromine (JSC Vekton, chemically pure) and elemental fluorine obtained directly in the laboratory using a fluorine cell with consequent purification on sodium fluoride. The obtained product was distilled using the technique described in Ref. [14], and stored in tightly closed PTFE containers. It was distilled again immediately before the synthesis of KBrF$_4$.

2.2. Synthesis of KBrF$_4$

KBrF$_4$ was synthesized in three-component heterogeneous system containing solid potassium fluoride (JSC Vekton, analytical grade) and two non-mixing liquids: bromine trifluoride and Freon-113 (Roskholoda Ltd., technical grade). The technique is described in our previous studies [9,10].

2.3. Interaction between iridium metal and molten KBrF$_4$

The reaction was carried out in a glass-carbon crucible at the temperature of 673 K under argon atmosphere. The average mass of KBrF$_4$ in the mixture was 5 g so that the mass ratio of Ir:KBrF$_4$ was close to 1:10 (1:9.85 by moles).

After the interaction the crucible was cooled, the product was hydrolyzed in water, and the surface area of the clean iridium sample was measured using a vernier caliper.

2.4. Interaction between iridium metal and KBrF$_4$ dissolved in BrF$_3$

This series of experiments was performed in PTFE crucibles in isothermal conditions at 373, 388 and 403 K at various times of the process (up to 6 hours). KBrF$_4$ was formed *in situ*. The fivefold excess of bromine trifluoride was used to prevent the formation of bromine monofluoride as well as to maintain the enough amount of liquid medium for dissolving the reaction products.

A sample of iridium was put into a crucible; KF and BrF$_3$ were added in a mass ratio of Ir:KF:BrF$_3$ = 1:1.21:5 (1:4.01:7.02 by moles). The pre-distillation of possible volatile impurities was performed by evacuation until the pressure was close to the vapor pressure of bromine trifluoride at 298 K (~0.01 bar). The crucible with the initial mixture was tightly closed with a PTFE stopper and inserted into a furnace at a fixed temperature. After 6 hours, the crucible was rapidly cooled, and the amount of dissolved iridium as well as its surface area was measured after sample cleaning according to the procedure described above.

3. Results and discussion

In this research we have studied kinetic dependencies for the two following processes: interaction of iridium metal with molten potassium tetrafluoridobromate, and with the solution of potassium tetrafluoridobromate in liquid bromine. The formal rate of transformation of iridium into its fluorinated derivative is accounted as a main quantitative characteristic for both experiments.

3.1. Interaction of molten potassium tetrafluoridobromate with iridium metal

In this series of experiments with different interaction times, the initial substances were mixed in a mass ratio of
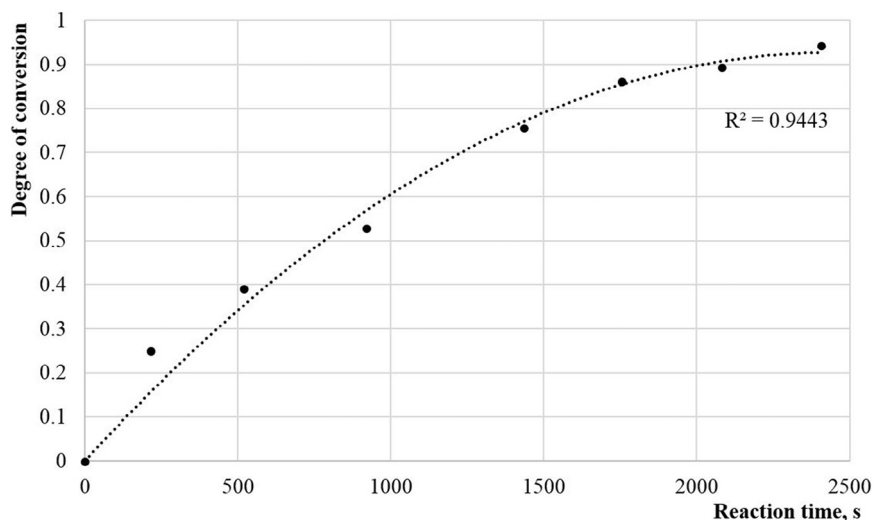
Fig. 1. Dependence of the degree of conversion of iridium on the reaction time.

Ir:KBrF$_4$ = 1:10 (1:9.85 by moles) and then heated up to 400 °C in the inert atmosphere. After each experiment, the conversion of iridium into its fluorinated derivative was calculated in terms of the degree of conversion, α. The obtained experimental data are shown in Fig. 1 as a dependence of the degree of conversion on the reaction time.

The data were then mathematically processed using common rate equations applicable to heterogeneous reactions [15]. After linearization of the experimental kinetic curve, it was revealed that the best correspondence takes place in the case of contracting envelope Eq. (2), as presented in Fig. 2.

$$1-(1-\alpha)^{1/3} = k\tau \tag{2}$$

where α is the degree of conversion of iridium; k is the reaction rate constant, s^{-1}; τ is the reaction time, s.

This model adequately describes the kinetics of the studied reaction between iridium metal and KBrF$_4$ demonstrating the best R-factor of approximation (Fig. 2). It strongly suggests

that reaction products dissolve in the excess of the tetrafluoridobromate, and therefore, there is no significant diffusional resistance in the reaction mixture. The value of reaction rate constant at 673 K is $(2.51 \pm 0.08) \cdot 10^{-4}\,\text{s}^{-1}$.

In this way, the dependence of the degree of conversion on the reaction time at 673 K can be described by the following equation:

$$\alpha = 1-\left(1-\exp\left(2.51\cdot10^{-4}\cdot\tau\right)\right) \tag{3}$$

The rate of iridium fluorinated on the surface of metal by molted KBrF$_4$ is represented by the ratio between mass loss of iridium during the experiment and surface area of the initial iridium sample (estimated using a precise vernier caliper) multiplied by the total time of the process

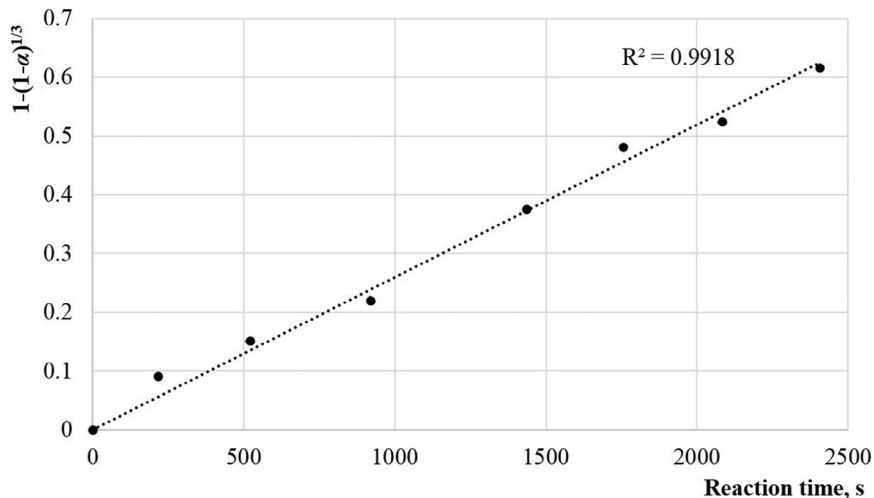$$R_d = \frac{\Delta m(Ir)}{S_{surf}(Ir)\Delta\tau} \tag{4}$$

Fig. 2. Linearization of kinetic data on reaction of iridium with KBrF$_4$ at 673 K using contracting envelope rate equation.
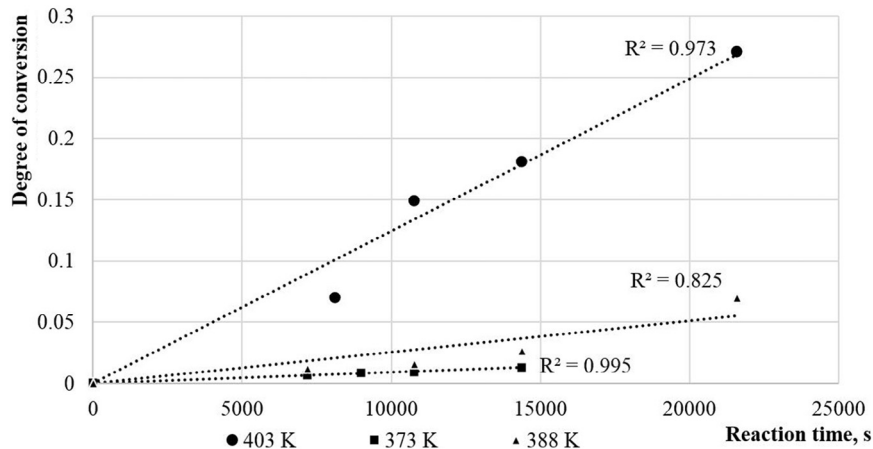
Fig. 3. Dependence of the degree of conversion of iridium on the reaction time.

where R_d is the rate of iridium fluorination, g/(dm^2·h); Δm(Ir) is the mass loss of iridium, g.; S_{surf}(Ir) is the surface area of the initial iridium sample, dm^2; $\Delta \tau$ is the time interval (short enough to assume that the surface area is constant), h.

A rough estimation of the reaction rate of iridium in molten KBrF$_4$ on the surface of metal gives a value not less than 100 g/dm^2·h at 673 K (a more precise determination was complicated by slight etching of Ir surface). The high reaction rate of iridium metal fluorination allows fast transformation of iridium into its soluble form, K$_2$IrF$_6$, for further recovery.

3.2. Interaction of solution of potassium tetrafluoridobromate in liquid bromine trifluoride with iridium metal

Besides molten KBrF$_4$, we investigated the possibility of application of solutions of KBrF$_4$ in liquid BrF$_3$ at lower temperatures. As a result of the studies, the set of experimental data describing the dependence of the degree of conversion on the reaction time and temperature was obtained.

The experimental data are shown in Fig. 3 as a dependence of the degree of conversion (α) on the reaction time (τ) at different temperatures.

In this case, linear approximation was used on the analogy with the interaction of iridium metal with molten potassium tetrafluoridobromate. For low values of the degree of conversion (up to 30%), the dependence can be described by a straight line as it is very unlikely that the reaction plateau is reached in the vicinity. However, the experiments were not carried out up to steady-state regime for practical reasons because such a time-consuming process (more than 5 hours) is desired neither for analytical nor for industrial applications.

The data were then mathematically processed using the same techniques as described in Section 3.1. The contracting envelope equation has also demonstrated the best correspondence (Fig. 4).

The dependence of the reaction rate of iridium dissolving in the solution of KBrF$_4$ in liquid bromine trifluoride on the
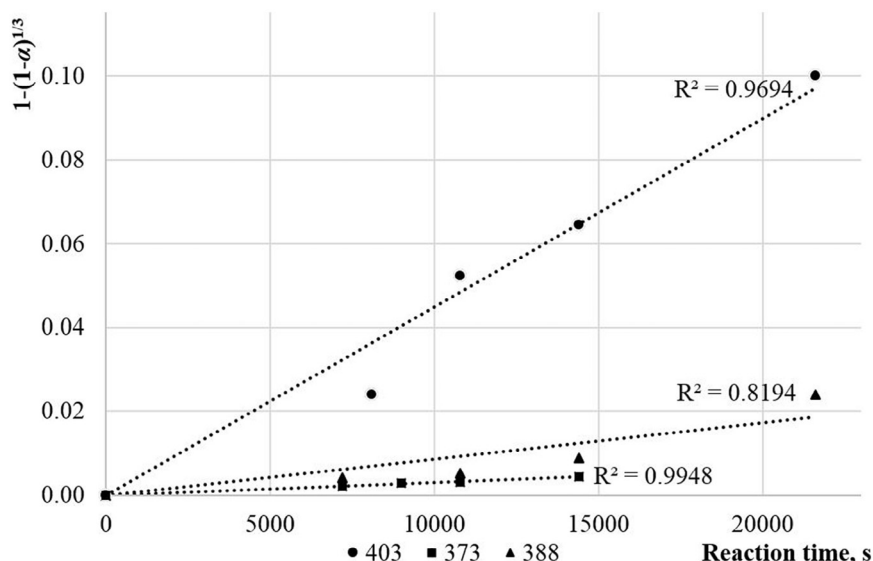

Fig. 4. Linearization of kinetic data of iridium metal dissolving in the mixture of BrF$_3$ and KBrF$_4$ using contracting envelope rate equation.
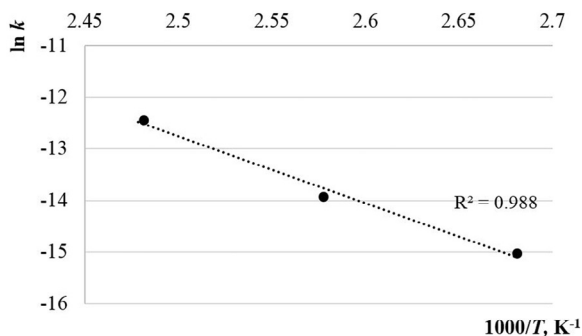
Fig. 5. Dependence of reaction rate of iridium dissolving in $KBrF_4$–BrF_3 solution on reciprocal temperature.

reciprocal temperature in axes of Arrhenius equation (Eq. (5)) is shown in Fig. 5.

$$\ln k_T = \ln k_0 - E_a/RT \qquad (5)$$

where k_T is the reaction rate constant, k_0 is the pre-exponential factor, E_a is the apparent energy of activation.

As it follows from the pattern in Fig. 5, $\ln k_0 = -12.947$, and $k_0 = 2.38 \cdot 10^{-5}$. Using the slope of the straight line, the apparent activation energy of interaction of iridium with the solution of $KBrF_4$ in bromine trifluoride can be calculated: $E_a = (107 \pm 12)$ kJ/mole. It suggests that the process of iridium fluorination is a kinetically controlled reaction, i.e. the process is mainly limited by chemical interaction rather than by diffusion. Such a kinetically controlled reaction can be intensified by increasing temperature.

Using the values obtained above, the dependence of the degree of conversion on the reaction time can be formulated in a form of the following equation

$$\alpha = 1 - \left(1 - \exp(-107000/RT) \cdot 2.38 \cdot 10^{-5} \cdot \tau\right)^3 \qquad (6)$$

where α is the degree of conversion, R is the universal gas constant, T is the temperature and τ is the reaction time.

The rate of iridium metal dissolving on its surface in the solution of $KBrF_4$ in BrF_3 reaches only 2.18 g/(dm^2·h) at 403 K. In contrast, the reaction rate of iridium fluorination in $KBrF_4$ melt is significantly higher than in $BrF_3 - KBrF_4$ solution which can be explained by higher temperature as well as by changing the nature of the solvent in the system.

4. Conclusions

The obtained results show the principal possibility of express and convenient transformation of compact iridium metal into its soluble form by means of interaction with $KBrF_4$.

When the two experiments with different conditions and fluorination agents are compared, it turns out that iridium reacts almost 50 times faster in molten $KBrF_4$ than in $KBrF_4$–BrF_3 solution. Usage of BrF_3 solutions is limited by its boiling point, which makes molten $KBrF_4$ a more preferable fluorinating agent at higher temperatures.

Further recovery of iridium in a pure form can be carried out in several possible ways, for example, by dissolving in diluted (1%) hydrochloric acid [13]. Further investigations on this subject are ongoing.

References

[1] E. White, R. Singh, Patent Landscape Report on E-Waste Recycling Technologies, Thomson Reuters IP Analytics, 2013.

[2] S. Dey, J. Takaranta, E-waste recycling technology patents filed in India – an analysis, J. Intellect. Prop. Rights 19 (2014) 315–324.

[3] A. Tsamis, M. Coyne, Recovery of Rare Earths from Electronic Wastes: An Opportunity for High-Tech SMEs, Centre for Strategy and Evaluation Services LLP, 2015.

[4] H. Dong, J. Zhao, J. Chen, Y. Wu, B. Li, Recovery of platinum group metals from spent catalysts: a review, Int. J. Miner. Process 145 (2015) 108–113.

[5] R. Kahhat, E-waste Management: From Waste to Resource, Routledge, 2012.

[6] K. Zhang, Recycling of Electronic Waste II: Proceedings of the Second Symposium, John Wiley & Sons, 2011.

[7] Recycling Rates of Metals: A Status Report, UNEP International Resource Panel, 2011.

[8] V.N. Mitkin, Physical–chemical basis for application of fluoroxidants in noble metal analytical chemistry, Spectrochim. Acta Part B At. Spectrosc. 56 (2001) 135–175.

[9] S.I. Ivlev, A.J. Karttunen, R.V. Ostvald, F. Kraus, RbBrF$_4$ revisited, Z. Anorg. Allg. Chem. 641 (2015) 2593–2598.

[10] S.I. Ivlev, P. Woidy, V. Sobolev, I. Gerin, R. Ostvald, F. Kraus, On tetrafluorobromates(III): crystal structures of the dibromate CsBr$_2$F$_7$ and the monobromate CsBrF$_4$, Z. Anorg. Allg. Chem. 639 (2013) 2846–2850.

[11] S.I. Ivlev, P. Woidy, F. Kraus, I.I. Gerin, R.V. Ostvald, Tetrafluorobromates for urban mining of noble metals: a case study on iridium metal, Eur. J. Inorg. Chem. 2013 (2013) 4984–4987.

[12] V.N. Mitkin, Fluorination of Iridium Metal and Its Application Possibilities in the Synthesis, Analysis and Recovery Technology for Secondary Raw Materials (Review), Iridium: Proc. Intern. Symp., TMS-2000, Nashville Tennessee, 2000, 377–390.

[13] V.V. Shagalov, Physical-Chemical Basis of Potassium Tetrafluoridobromate Synthesis, Tomsk Polytechnic University, 2010.

[14] I.I. Gerin, G.N. Amelina, V.V. Gordienko, R.V. Kalajda, V.F. Usov, A.Y. Vodyankin, et al., Volumetric properties of IF$_5$ and BrF$_3$. The message 2. Saturated vapour pressure of bromine trifluoride, Bull. Tomsk Polytech. Univ. 305 (2002) 263–273.

[15] C. Popescu, Integral method to analyze the kinetics of heterogeneous reactions under non-isothermal conditions. A variant on the Ozawa-Flynn-Wall method, Thermochim. Acta 285 (1996) 309–323.