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PRODUCTION OF HIGHER FLUORIDES OF PLATINUM GROUP METALS IN ANHYDROUS SOLVENTS

V. B. Sokolov, Yu. V. Drobyshevskii,
V. N. Prusakov, A. V. Ryzhkov,
and S. S. Khoroshev

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It is known [1] that krypton difluoride is a strong fluorination agent and exhibits the classic characteristics in complex formation reactions (it acts as a fluorine ion donor). Krypton difluoride is thermally unstable [2]. Complex KrF_2 compounds and many inorganic fluorides can be produced only by the anhydrous solvents method. The applications of this method are examined in this work based on the reaction of KrF_2 with platinum group metals. The most suitable solvents for carrying out the oxidative fluorination and KrF_2 complex formation are bromine pentafluoride and anhydrous hydrogen fluoride. Solvents such as ClF_3 , BrF_3 , and IF_5 are oxidized by KrF_2 to higher fluorides and the solubility of KrF_2 in ClF_5 and IF_7 is low. Chemically inert to bromine pentafluoride and HF, KrF_2 is quite soluble (~ 2010 g $KrF_2/1000$ g BrF_5 and ~ 1950 g $KrF_2/1000$ g HF) [3], so that a significant concentration of KrF_2 can exist in the reaction vessel. This produces homogeneous solutions in the case of the complex forming reaction (many fluoric acids are also easily soluble in BrF_5 and HF). Complex compounds of the desired composition can, thus, be produced. The effect of the solvent on the rate of the heterogeneous fluorination reaction ($Me + KrF_2$, $Me_nO_m + KrF_2$, $Me_nF_m + KrF_2$, etc.) is mainly the creation of optimum KrF_2 concentrations on the solid surface.

Synthesis is carried out as follows. The sample is placed in the reaction vessel, the reactor is sealed, and is connected to the startup vacuum system. Solvent and then KrF_2 are condensed in the reactor which is cooled by liquid nitrogen. The reactor is then heated to -40° to $+25^\circ C$, depending on the fluoride being synthesized. The reaction is monitored by the pressure of the krypton evolved. Separation of the solvent-hexafluoride is difficult, unlike the solvent-platinum group metal-pentafluoride system. Platinum group metal hexafluorides are therefore produced after separation of complex compounds of KrF_2 and metal pentafluoride.

The reaction of KrF_2 with the platinum group metal pentafluorides in the KrF_2 solutions forms complex compounds (composition $KrF_2 \cdot MF_5$ ($M = Pt, Ru, Rh$) and $KrF_2 \cdot 2MF_5$ ($M = Pt, Ru$)). These can be separated after solvent distillation below $0^\circ C$. Frequencies characteristic for MF_5^- and $M_2F_{11}^-$ anions are observed in Raman effect spectra of the compounds produced. Typical spectra of $KrF_2 \cdot MF_5$ and $KrF_2 \cdot 2MF_5$ are shown in Fig. 1 for ruthenium related to the $Kr-F$ stretching vibrations in a KrF^+ diatomic ion. There are some deviations from the symmetry pairing rule O_h which is characteristic for 1:1 composition compounds. These are explained by the reduced symmetry of the anion in the crystal caused by ion interaction and the formation of cross-linkage bonds. The compounds produced can therefore be considered as $KrF^+MF_5^-$ and $KrF^+M_2F_{11}^-$ in the framework of the ionic model.

The compounds formed at $0^\circ C$ are crystalline substances with no appreciable dissociation pressure. Their coloring is similar to that of the corresponding pentafluorides but is not as strong. They are prone to rapid hydrolysis accompanied by acidification of water. They are unstable in anhydrous solvents. Decomposition of

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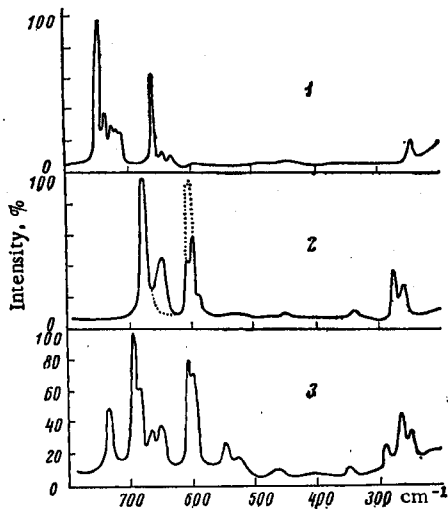


Fig. 1

Fig. 1. Raman effect spectra of ruthenium fluorides (He-Ne laser, $\lambda = 6328 \text{ \AA}$, $t < 0^\circ\text{C}$: 1) RuF_5 ; 2) $\text{KrF}^+\text{RuF}_6^-$; 3) $\text{KrF}^+\text{RuF}_{11}^-$.

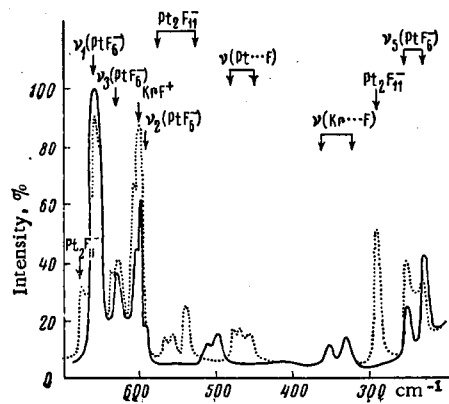
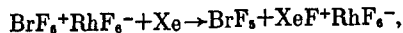


Fig. 2

Fig. 2. Raman effect spectra of $\text{KrF}_2 \cdot \text{PtF}_5$ and $\text{KrF}_2 \cdot 2\text{PtF}_5$ (dotted curve) (He-Ne laser, $\lambda = 6328 \text{ \AA}$, $t < 0^\circ\text{C}$).

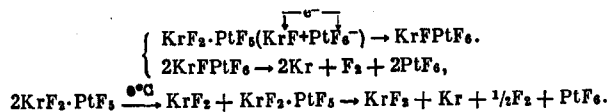
the compound in BrF_5 is accompanied by oxidation of BrF_5 to BrF_6^+ . This is confirmed by spectral investigations. Compounds thus formed are weaker oxidizing agents than the corresponding KrF_2 compounds but can oxidize Xe and O_2 :



It is possible that the instability of KrF_2 complex compounds in HF is caused by reaction with the solvent, e.g.:



Slight heating of $\text{KrF}_2 \cdot \text{MF}_5$ type compounds results in their vigorous dissociation with practically quantitative yield of the corresponding hexafluorides [4]. The following reaction sequence, including intramolecular oxidation-reduction,



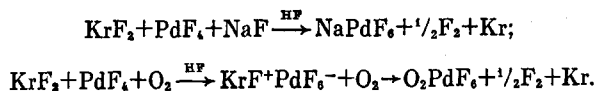
adequately explains these results and the data on compound structure. The Raman effect spectrum shown in Fig. 2 confirms the possibility of representing these complex compounds in the framework of an ionic model. Formation of platinum hexafluoride corresponds to time-proportional reduction of intensity of all observed absorption bands in the spectrum. A relatively long induction period is also characteristic for this process. No vaporization of platinum hexafluoride is observed during this period.

Stability of these KrF_2 compounds is determined by the following relationship between the energy of the crystalline lattice U , affinity for an electron E , and ionization potential I :

$$U_{\text{KrF}^+ \text{MF}_6^-} + I_{\text{MF}_6^-} + E_{\text{KrF}^+} > 0$$

Analysis shows that for all the above compounds $-E_{\text{KrF}^+} (305-310 \text{ kcal/mole}) > U_{\text{KrF}^+ \text{MF}_6^-} + I_{\text{MF}_6^-} (\leq 300 \text{ kcal/mole})$. The relationship for the corresponding gold compound $\text{KrF}_2 \cdot \text{AuF}_5$ is $-E \leq U + I$, so that it must be stable to anion oxidation. This is confirmed experimentally: $\text{KrF}^+ \text{AuF}_6^-$ decomposes at $65-70^\circ\text{C}$ forming gold pentafluoride [5]. Compounds of osmium and iridium show $U + I \leq -E$. Their decomposition forming hexafluorides occurs below 0°C and the corresponding complex compounds are stable only below -60°C .

Palladium pentafluoride is unknown. Metallic palladium easily reacts with KrF_2 in the above solvents forming a tetrafluoride which is insoluble in BrF_3 and HF . The solutions are dark-red colored when there is an excess of KrF_2 . It has been hypothesized that palladium(V) fluoride is formed based on the higher solubility of platinum group metal pentafluorides with higher KrF_2 concentration in the solution. However it proved impossible to produce pure PdF_5 : PdF_4 crystallized from the solution as KrF_2 concentration was reduced by the reaction. Distilling the solvent at low temperatures also does not result in stabilization of Pd(V) due to formation of $\text{KrF}^+\text{PdF}_6^-$. Introduction of NaF and O_2 in the reaction mixture stabilized Pd(V) . The following reactions take place with an excess of KrF_2 :



Palladium valence in the yellowish-brown reaction product was confirmed by studying its Raman effect spectra. A reactive intermediate product NaPdF_6 is formed. It acidifies the water and slowly decomposes forming Pd(IV) .

Oscillation frequencies (cm^{-1}) of NaPdF_6 and some other stable compounds of Pd(IV) and Pd(V) are tabulated with frequencies of rhodium compounds for comparison:

NaPdF_6	— 642 (100) $\nu_1\text{PdF}_6^-$, 566 (5) $\nu_2\text{PdF}_6^-$, 267 (28) $\nu_3\text{PdF}_6^-$.
Cs_2PdF_6	— 561 (100) $\nu_1\text{PdF}_6^{2-}$, 238 (34) $\nu_3\text{PdF}_6^{2-}$.
O_2PdF_6	— 645 (100) $\nu_1\text{PdF}_6^-$, 569 (18) $\nu_2\text{PdF}_6^-$, 265 (31) $\nu_3\text{PdF}_6^-$, 1817 (54) O_2^+ .
$(\text{XeF}_5^+)_2\text{PdF}_6^{2-}$	— 563 (100) $\nu_1\text{PdF}_6^{2-}$, 240 (23), 225 (12) $\nu_3\text{PdF}_6^{2-}$, 659 (117), 651 (128), 604 (102), 595 (91) XeF_5^+ .
NaRhF_6	— 638 (100) $\nu_1\text{RhF}_6^-$, 261 (23) $\nu_3\text{RhF}_6^-$.
O_2RhF_6	— 648 (100) $\nu_1\text{RhF}_6^-$, 575 (16) $\nu_2\text{RhF}_6^-$, 263 (29) $\nu_3\text{RhF}_6^-$, 1825 (80) O_2^+ .

The observed frequencies are expressed relative to octahedral MF_6^- and MF_6^{2-} characteristic frequencies. Absorption band intensities (in relative units) are shown in brackets.

The results of this work show, in our opinion, the extensive applicability of this method of producing higher fluorides of platinum group metals. Platinum, ruthenium, and rhodium hexafluorides are usually synthesized under high temperature and pressure (400°C, 300–400 abs atm) with $\leq 50\%$ yield [6]. We were able to synthesize pure PrF_4 [7], CrF_5 , previously unknown AuF_5 [5], NpF_5 , and NpOF_5 [8], and other inorganic fluorides by using KrF_2 solutions in BrF_3 and anhydrous HF at room temperature. This method was also successfully applied to produce complex compounds of KrF_2 with pentafluorides of IV and V group metals, to stabilize AgF_3 , and to study the mechanism of chemical reactions. The proposed method [9] for stabilizing ArF^+ by forming unknown $\text{ArF}^+\text{PtF}_6^-$ as a result of thermolysis of a mixture of argon, fluorine, and platinum hexafluoride does not appear to be promising based on the results obtained and the evaluation of stability in the series $\text{RnF}_2-\text{XeF}_2-\text{KrF}_2-\text{ArF}_2$ and $\text{RnF}^+-\text{XeF}^+-\text{KrF}^+-\text{ArF}^+$.

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