A STUDY OF THE HYDROLYSIS OF ZrF$_6^{2-}$ AND THE STRUCTURE OF INTERMEDIATE HYDROLYSIS PRODUCTS BY $^{19}$F AND $^{91}$Zr NMR IN THE 9.4 T FIELD

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The high-field $^{19}$F and $^{91}$Zr NMR method is used to study the hydrolysis and polycondensation of hexafluorozirconate ZrF$_6^{2-}$ in aqueous and water-peroxide solutions. During hydrolysis in aqueous solutions only ZrF$_6^{2-}$ and F$^-$ ions were observed by NMR, however, in the water-peroxide medium, an intermediate product of hydrolysis ([F$_5$Zr--OO--ZrF$_5$]$^{4-}$ dimer) was detected. The dimer structure is confirmed by $^{19}$F and $^{91}$Zr NMR. In high fields ($^{19}$F NMR frequency $>$ 200 MHz), the fluorine exchange between ZrF$_6^{2-}$ and F$^-$ is slow in the $^{19}$F NMR scale and has a multisite character.

Keywords: Zr(IV), fluorides, fluoride complexes, hydrolysis, polycondensation, $^{19}$F and $^{91}$Zr NMR.

INTRODUCTION

Solid phases of zirconium hexa- and heptafluorides were first described by C. Marignac 150 years ago [1], however, only the [ZrF$_6$]$^{2-}$ ion was found in their aqueous solutions, while the [ZrF$_7$]$^{3-}$ ion itself has not been found so far. Paper chromatography and electrophoresis of solutions of pent-, hexa-, and heptafluorozirconates labelled with $^{95}$Zr showed that the only mononuclear form of zirconium is [ZrF$_6$]$^{2-}$ in them [2].

The NMR method is one of the most informative methods to determine the structure of forms in solutions, however, in the $^{19}$F NMR spectra at 15-75 MHz NMR frequencies of zirconium heptafluoride solutions as well as К$_2$[ZrF$_6$] + К$_2$[HfF$_6$] solutions, one $^{19}$F NMR peak was observed, the position of which depended on the ratio of components [3-5]. This indicated fast or intermediate fluorine exchange in the NMR time scale and gave evidence of the lability of anions in aqueous solutions at room temperature.

It is possible to slow down the exchange in solutions by a substantial decrease in temperature, however, the temperature decrease in aqueous solutions is limited by their freezing at about 0°C. High field measurements (frequencies $\geq$200 MHz) make the condition of fast exchange more rigid and one may hope for separate recording of peaks with different shapes.

An acid reaction of hexafluorozirconate (HFZ) solutions indicates the hydrolysis of the ZrF$_6^{2-}$ ion. A study of HFZ hydrolysis is not only of the fundamental importance, but also of practical interest. Details of the only potentiometric study of ZrF$_6^{2-}$ hydrolysis [6] were not published. At the same time, we do not know the data on the solubility of the products of...
Zr$^{2-}$ hydrolysis, though one may try to find them in the NMR $^{19}$F spectra. Using the latter and that ZrF$_6^{2-}$ is one of few forms observed in $^{91}$Zr NMR [7], we have initiated the study of ZrF$_6^{2-}$ hydrolysis by $^{19}$F and $^{91}$Zr NMR.

**EXPERIMENTAL**

The samples of solutions with a hexafluorozirconate concentration of 0.04-0.1 mol/l were prepared from potassium and cesium salts in a Teflon dish by dissolving the reagents in water or aqueous (30%) solution of hydrogen peroxide. For neutralization we used 1M NaOH or 1-1.4M KOH solutions.

The $^{19}$F and $^{91}$Zr NMR spectra were measured on a MSL-400 Bruker NMR spectrometer at frequencies of 376.5 MHz and 37.2 MHz with the cumulative frequency of 0.2 Hz and 18 Hz respectively at a temperature of 295±3 K at the natural isotope content. $^{19}$F chemical shifts (CS, $\delta$) are given from CFCl$_3$ using the CF$_3$COOH solution as the external reference ($\delta = -79$ ppm from CFCl$_3$), which was placed coaxially in a capillary inside the tube with the sample; peak intensities were compared with the intensity of the same reference. The $^{91}$Zr NMR spectra were measured on a high power probe using Teflon NMR tubes with a diameter of 10 mm. The $^{91}$Zr CS was counted from the peak of 0.1M aqueous solution of Cs$_2$ZrF$_6$ taking it to be $-191$ ppm from Cp$_2$ZrBr$_2$ [7]. The fluorine concentrations were determined by comparing the integral intensities of the reference peak and the observed peaks of forms in the spectra.

**RESULTS AND DISCUSSION**

In order to test the possibility of separate observation of different chemical forms at an NMR frequency of 376 MHz, the $^{19}$F NMR spectrum of aqueous solutions of K$_2$ZrF$_6$ and K$_2$HfF$_6$ was measured in the presence of KF (Fig. 1). It showed that the peaks of these ions and F$^-$ were observed separately, unlike the data [3, 4] obtained at frequencies of 15 MHz to 40 MHz. The assignment of peaks of ZrF$_6^{2-}$ and HfF$_6^{2-}$ ions was made by comparing them with the spectra of solutions of individual K$_2$ZrF$_6$ and K$_2$HfF$_6$ salts.

In the $^{19}$F NMR spectra of aqueous solutions of HFZ, the peak width is strongly dependent on the presence of the excess fluoride ion F$_{exc}$ with respect to stoichiometry of ZrF$_6^{2-}$. This means that the peak width has an exchange character, and hence, the stock solution contains a small concentration of fluoride whose $^{19}$F NMR peak does not exceed the noise level of the experiment.

Stock solutions had pH $\sim$ 4, which indicates the hydrolysis of ZrF$_6^{2-}$ in the aqueous medium; However, the released fluoride ion is not observed in the spectrum because of the low concentration ($\sim 10^{-4}$ mol/l) and a very wide peak.

This means that the process

$$\text{ZrF}_6^{2-} + \text{H}_2\text{O} \xrightleftharpoons{k_1} \text{ZrF}_3\text{H}_2\text{O}^- + \text{F}^- \rightarrow \text{ZrF}_5\text{OH}^{2-} + \text{F}^- + \text{H}^+$$

(1)

proceeds insignificantly, and the formed aqua acid is weak or moderate. It is possible to shift the equilibrium to the right by changing the pH of the solution.

The NMR spectrum of 0.1M solution of Cs$_2$ZrF$_6$ with the addition of NaOH in the ratio $Z = \text{OH}/\text{Zr} = 0.5$ is given in Fig. 2; the NMR data for the K$_2$ZrF$_6$ solution with the addition of KOH are given in Table 1. Concentrations of fluorine in HFZ and fluoride ions are given in Table 1 with allowance for a change in the volume of solutions due to the addition of alkali.

When alkali is added to aqueous solutions containing the ZrF$_6^{2-}$ ion, the peaks of only ZrF$_6^{2-}$ and F$^-$ ions are observed in the NMR spectra of fluorine; the other forms were not detected. As alkali was added, the ZrF$_6^{2-}$ concentration decreased, while the $^{19}$F NMR peak width of this ion increased (Table 1). Here the concentration of the fluoride ion increases,