

Hydrolysis in the system LiPF_6 —propylene carbonate—dimethyl carbonate— H_2O

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Abstract

¹⁹F and ³¹P NMR spectroscopy were used to study the kinetics of the hydrolysis of LiPF_6 in the homogenous solvent system propylene carbonate (PC)—dimethyl carbonate (DMC)— H_2O . It was found that the main products of the hydrolysis are HF, LiPO_2F_2 and $\text{Li}_2\text{PO}_3\text{F}$. The content of POF_3 and PF_5 was negligibly low. We set up a hypothesis that the main factor determining the rate of the process is the so-called 'secondary' catalytic effect, caused by solvated H^+ ions.

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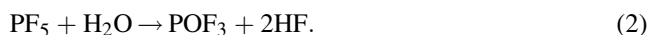
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1. Introduction

Solutions of lithium hexafluorophosphate in aprotic organic solvents are widely used as electrolytes in rechargeable lithium cells; see, e.g. [1–4]. Taking into consideration the high hygroscopicity of LiPF_6 , such systems are always contaminated with a certain amount of water that gives rise to hydrolysis of the complex fluoro anion. The products formed, especially HF, have a negative influence on the performance of lithium batteries. There are a number of publications dedicated to the problem of hydrolytic stability of the electrolytes containing lithium hexafluorophosphate, various aprotic solvents and water as well as to the use of water-binding additives [5–8]. At the same time, the reaction mechanism of the hydrolysis of LiPF_6 in the systems studied is not clear. It is usually supposed [6,9,10] that in the first stage of the reaction, the complex decomposes forming phosphorus pentafluoride and lithium fluoride



followed by the interaction between the phosphorus pentafluoride formed and water,



Despite the fact that the data on the thermal stability of LiPF_6 are somewhat contradictory [11–15], both literature data and our experimental evidence indicate that, at room temperature, the decomposition of LiPF_6 , producing gaseous phosphorus pentafluoride and solid lithium fluoride according to Eq. (1), is negligible. However, the equilibrium of the process discussed could be shifted to the right due to the interaction between PF_5 and the solvent [6,13,16,17], and in this case, the above-mentioned mechanism cannot be excluded. Quantum chemical calculations [6,18] show the significance of the polarizing influence of Li^+ ions on the first coordination sphere of the complex anion. As a result, both the thermal and the hydrolytic stability of LiPF_6 are lowered, compared with hexafluorophosphates of other alkali metals.

At the same time, our estimation of the influence of Li^+ ions on the kinetics of the hydrolysis of PF_6^- and other fluoride complexes [19–22] allowed us to doubt that the low hydrolytic stability of LiPF_6 in aprotic solvents contami-

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nated by water is caused solely by the direct influence of Li^+ ions which initiate the mechanism of hydrolysis suggested in [6,9,10]. In this paper, we made an attempt to use ^{19}F and ^{31}P NMR spectroscopy to study the hydrolysis of LiPF_6 in a PC/DMC mixture containing 0.5% of water, and to put forward a hypothesis about the reaction mechanism.

2. Results and discussion

In Fig. 1, are presented typical ^{19}F (Fig. 1a) and ^{31}P (Fig. 1b) NMR spectra of the solutions containing the starting material (LiPF_6) and the products of its hydrolysis. The ^{19}F spectra consist of the typical doublets with chemical shifts, $\delta_{\text{F}} = -72.4$ ppm [$J(\text{P},\text{F}) = 708$ Hz] that is assigned to PF_6^- , -76.7 ppm [$J(\text{P},\text{F}) = 934$ Hz] (PO_3F^{2-} , but see below), and -83.8 ppm [$J(\text{P},\text{F}) = 975$ Hz] (PO_2F_2^-), as well as the singlet with $\delta_{\text{F}} = -153.7$ ppm belonging to HF. The intensities of the signals of other P–F compounds that could possibly be assigned to either POF_3 or solvated PF_5 are

much lower. The signal assignments are based both on literature data [23–25] and on the analysis of the ^{31}P NMR spectra. The latter contain a septet with $\delta_{\text{P}} = -146.1$ ppm [$J(\text{P},\text{F}) = 708$ Hz] belonging to PF_6^- , a triplet with $\delta_{\text{P}} = -21.6$ ppm [$J(\text{P},\text{F}) = 975$ Hz] (PO_2F_2^-), a doublet with $\delta_{\text{P}} = -10.1$ ppm [$J(\text{P},\text{F}) = 934$ Hz] (PO_3F^{2-}) as well as a singlet attributed to H_3PO_4 that could be formed in the final stage of the hydrolysis. The intensities of the other signals are too low to be clearly seen in the spectra. Thus, we found that among the fluorine-containing products of the hydrolysis, only PO_2F_2^- , PO_3F^{2-} and HF are present in significant amounts; the content of POF_3 (or solvated PF_5) is considerably lower.

We performed a check on the identity of PO_3F^{2-} by recording ^{19}F and ^{31}P NMR spectra of $\text{Na}_2\text{PO}_3\text{F}$ using PC/DMC (1:1) plus a few drops of water as the solvent. Acetone- d_6 /H $_2$ O (2:1) was also used because it provided better solubility for $\text{Na}_2\text{PO}_3\text{F}$ and gave similar NMR data: $\delta_{\text{F}} = -72.3$ ppm, $\delta_{\text{P}} = +2.6$ ppm, $J(\text{P},\text{F}) = 868$ Hz. These values do not agree well with those of the signals assigned

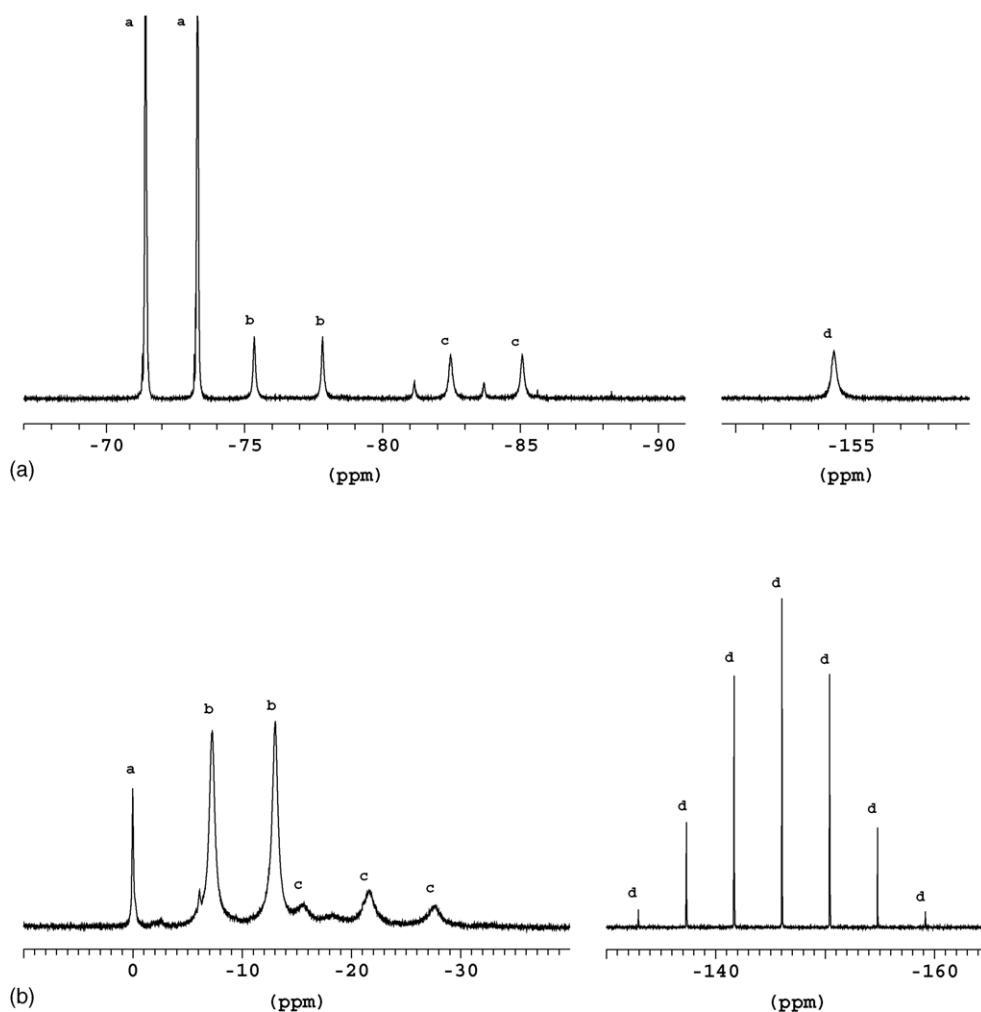


Fig. 1. Typical ^{19}F and ^{31}P NMR spectra of the solutions containing LiPF_6 and the products of its hydrolysis. (a) Signals a, b, c and d are assigned to PF_6^- , PO_3F^{2-} , PO_2F_2^- and HF, respectively. (b) Signals a, b, c and d belong to H_3PO_4 (probably), PO_3F^{2-} , PO_2F_2^- and PF_6^- , respectively.

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