



A Detailed Investigation of the Thermal Reactions of LiPF₆ Solution in Organic Carbonates Using ARC and DSC

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The thermal stability of 1 M LiPF₆ solutions in mixtures of ethylene carbonate, diethyl carbonate, and dimethyl carbonate in the temperature range of 40 to 350°C was studied by accelerating rate calorimeters (ARC) and differential scanning calorimeters (DSC). Nuclear magnetic resonance (NMR) was used to analyze the condensed reaction products at different reaction stages. Studies by DSC and pressure measurements during ARC experiments with LiPF₆ solutions detected a gas-releasing endothermic reaction starting at ~170°C, involving diethyl carbonate which occurs before a number of exothermic reactions, which follow as the temperature increases. Fluoride ions are released and react with the alkyl carbonate molecules both as bases and as nucleophiles. The bulk analysis by NMR shows that HO-CH₂-CH₂-OH, FCH₂CH₂-OH, F-CH₂CH₂-F, and polymer are major products. Gas analysis by NMR and Fourier transform infrared spectroscopy shows PF₅, CO₂, CH₃F, CH₃CH₂F, and H₂O as major gaseous products of the thermal reaction of these solutions.

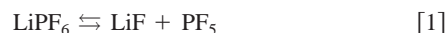
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During the past three decades, lithium ion batteries have become a dominant rechargeable power source for portable electronic devices. Lithium ion technology is advancing rapidly and major improvements are focusing on battery capacity and safety. In addition, the growing desire in recent years to utilize these high performance lithium ion batteries for electric vehicle (EV) and other large-sized equipment applications generates increasing safety concerns. Among developments for overcharge protection in these systems one may mention shutdown mechanism by separators, which melt at elevated temperatures and shut down internal conductivity in the battery, chemical shuttles, safety valves, and protective electronic circuits.¹⁻⁴ The safety of lithium ion cells is related mainly to the thermal reactivity of the materials in the cell. When the temperature of a lithium ion battery is raised as a result of abusive conditions, (e.g., short circuit, overcharge, heating) a process of self-heating may be initiated. Various exothermic and endothermic reactions involving both the solution and the electrodes can then occur inside the cell. Possible processes contributing to self-heating include reactions between electrolyte and electrode materials and decomposition of the electrolyte solution due to reactions between salt and solvent. (All the salts relevant to Li-ion batteries have anions with atoms such as P, As, Cl, S in high oxidation states.) Heating resulting from chemical reactions and thermal decomposition can produce high pressure. The primary reaction products can be further involved in follow-up thermal reactions as the temperature rises. Therefore an understanding of the thermal behavior of the electrolyte solutions to be used is essential in the understanding of the safety features and the limitations of Li-ion batteries, and for the design of safe high performance batteries of this type.

The most common solvents used in Li-ion batteries are the alkyl carbonates, ethylene carbonate (EC), dimethyl carbonate (DMC), diethyl carbonate (DEC), and combinations thereof. So far the most common lithium salt used for 4 V Li-ion batteries has been LiPF₆, in spite of some of its disadvantages such as limited stability, unavoidable detrimental HF contamination of its solutions, and relatively high price. In spite of recent extensive efforts to develop alternative salts,⁵⁻⁹ LiPF₆ has remained the only electrolyte used in practical lithium ion batteries. Its merits include: (i) its high solubility in polar aprotic solvents, thus yielding highly conductive solutions; (ii) a wide electrochemical window and good anodic stability, (iii) acceptable safety features, it is nonexplosive and relatively

nonpoisonous. However, under appropriate conditions, LiPF₆ may be a source of the powerful Lewis acid PF₅ by way of the following equilibrium decomposition



Both the PF₅ and the fluoride ion may react with solution species (solvents). Furthermore, the P-F bonds are highly susceptible to hydrolysis by even trace amounts of moisture yielding HF and POF₃, etc. A rise in temperature will, of course, accelerate the formation of these species and their further reaction with the solvents. In investigations relating to the identity of decomposition products, Sloop *et al.* found that the reactions of LiPF₆ and of PF₅ with a 1:1 molar mixture of EC + DEC at 85°C both lead to discoloration, transesterification, and polycarbonate formation, as well as gaseous, unidentified products.¹⁰ Mori *et al.*¹¹ reported the products of thermal decomposition of LiPF₆/diisopropyl carbonate as (CH₃)₂CHF, CH₃CH = CH₂, (CH₃)₂CHOH, CO₂, and (CH₃)₂CHOCH(CH₃)₂. A recent, relatively extensive research, focusing on thermal phenomena but not identifying products, is that of Kawamura *et al.* who studied the behavior of solutions of LiPF₆ (1 M) in EC + DMC (1:1 v/v), in EC + DEC, in propylene carbonate (PC) + DMC and in PC + DEC, over a temperature range extending to above 300°C. For all cases they found exothermic peaks evidencing solvent decomposition below 285°C. For the mixed solvents containing DMC the peaks ranged from ~255-285°C with a maxima at ~270°C, whereas for the solvents containing DEC the peaks onsets and their maxima were ~15°C lower.¹² An earlier report of thermal behavior of relevance to the present work is that of Botte *et al.* relating to varying LiPF₆ concentrations and rate of heating, which were both found to affect the thermal stability of the alkyl carbonate solutions.¹³ Most of that work involved ethyl methyl carbonate (EMC) and EMC-EC mixtures. However both these studies were carried out using DSC only. The sensitivity of the DSC measurements depends greatly on the ratio of the heating and reaction rates, and they are less sensitive than measurements by accelerating rate calorimetry (ARC).^{14,15} In order to understand properly thermal stabilities of chemical systems at high temperature and to obtain good resolution of various reaction stages, both ARC and DSC should be used and accompanied by bulk product analysis.¹⁶⁻¹⁸

Herein we report a detailed investigation of the thermal behavior of solutions of LiPF₆ in a mixture of ethylene carbonate (EC), diethyl carbonate (DEC), dimethyl carbonate (DMC), using both ARC and DSC. Typically ARC has been used under adiabatic conditions to study thermal reactions by following temperature response.^{19,20}

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However, the nature of the technique is such that this permits the monitoring of exothermic reactions only. In the present study we have monitored both gas pressure and temperature responses and were thus also able to detect endothermic reactions in the absence of exotherm. DSC, in which heat flow permits the identification of both endothermic and exothermic reactions, was used to complement the data obtained from the studies by ARC. The products of the thermal reactions of these solutions were analyzed by Fourier transform infrared spectroscopy (FTIR), NMR, and gas chromatography-mass spectroscopy (GC-MS).

Experimental

The solutions EC:DEC:DMC, 2:1:2 by volume, containing 1 M LiPF_6 were obtained from Merck KGaA (highly pure, Li battery grade) and were ready for use. The water content of the solutions was less than 10 ppm as was measured by a Karl Fischer titrator (652KF-Coulometer, Metrohm, Switzerland). The boiling points of EC, DEC, and DMC at atmospheric pressure are 244, 128, and 90°C, respectively.

An accelerating rate calorimeter (ARC, Arthur D Little, Inc., model 2000) was operated in a heat-wait-search (HWS) mode until an exotherm is detected and adiabatic conditions were maintained until the completion of the exotherm. A differential scanning calorimeter (DSC, Mettler Toledo, Inc., model DSC 25) was used for measuring the heat flow rate of solution samples as a function of temperature.

In a typical test by ARC, 2 mL of the solution were placed in a titanium test cell (8 mL, from Arthur D. Little, Inc.) in a glove box under a highly purified Ar atmosphere, transferred to the calorimeter, and heated between 40 and 350°C with 5°C increments at the rate of 2°C/min in the search for self-heating at the sensitivity threshold of 0.02°C/min. The controller was programmed to wait 15 min for the sample and calorimeter temperatures to equilibrate, and then to search 20 min for a temperature increase of 0.02°C/min. At the end of the ARC experiments the pressure inside the test cells was relieved, and the test cells were transferred to a glove box for a further analysis of their content. In some experiments the gas accumulated in the test cell was collected for analysis.

DSC tests were carried out at different heating rates of 10, 5, 2, and 0.5°C/min in the temperature range 30-400°C. High-pressure gold-plated stainless crucibles, (Mettler Toledo, Switzerland) 30 μL in volume, were used in the DSC tests. The crucibles were loaded with three microliters of a sample and were closed in the glove box (VAC, Inc.). The weight of each sample (crucible + solution) was taken before and after the experiment to verify that the system was hermetically sealed. In all cases, the weight was constant indicating that there were no leaks during the experiments.

In control experiments, the behavior of the solvent mixture alone, in the absence of salt was studied.

We have used ^1H , ^{13}C , ^{31}P , and ^{19}F nuclear magnetic resonance, (NMR, Bruker, Inc., Instruments, AC-200, DPX-300, and DMX-600 NMR systems), and FTIR, (Nicolet Magna 860, Spectrometer placed in a glove box under H_2O and CO_2 -free atmosphere) to analyze the reaction products.

Samples of interest, either of the solvent mixture (EC:DEC:DMC, 2:1:2, v/v/v) or of the electrolyte solution (LiPF_6 , 1 M in the above mixed solvent) were heat-treated in the ARC apparatus and heating was stopped at different stages. After cooling, the liquid phase was subjected to NMR analysis. In selected cases the gas phase was collected by first cooling the test cell in liquid nitrogen until the pressure was reduced to 1 atm, and then the gas was released via a specially designed valve. For NMR analysis the gas was collected into CD_3CN solution. Gas sampled without liquid nitrogen cooling was contaminated by large amounts of H_2O .²¹

Results and Discussion

Figure 1 presents the DSC curve obtained for the solution of LiPF_6 in EC-DEC-DMC. It clearly indicates the existence of at least three reactions with heat effects. The first expresses itself as an

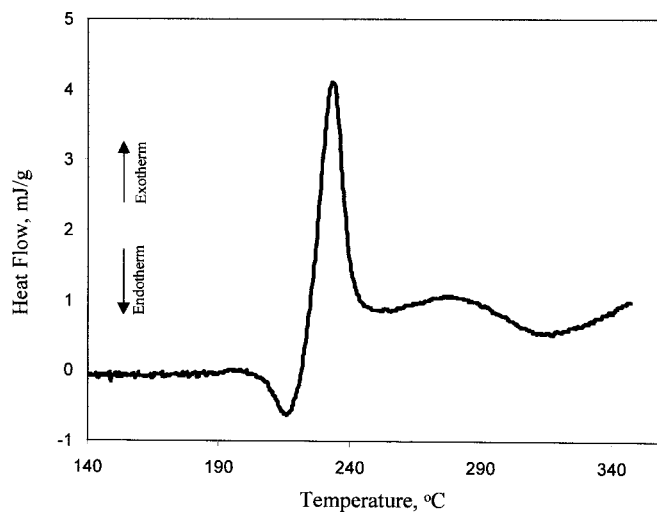


Figure 1. Typical DSC profile at the scan rate of 2°C/min for 1 M LiPF_6 -EC:DEC:DMC (2:1:2 v/v/v) electrolyte solution.

endothermic peak in the range 203-220°C with a heat of reaction of 37.6 J/g. It is followed by two exothermic peaks, a pronounced and relatively sharp one between 220 and 246°C with a heat of reaction of -395.7 J/g and a broad and lower one between ca. 250 and 310°C with a heat of reaction -100 J/g.

Figure 2 shows the real time curve of temperature and pressure changes measured in ARC experiments in the temperature range 40-350°C for an empty cell, a salt-free solvent mixture, and the LiPF_6 solution (indicated). The minor pressure increase below 170°C shown both by the solvent and by the electrolyte solution is, of course, due to the increase of vapor pressure of the solvent upon heating. At higher temperatures the salt-free solvent mixture enters a phase of significant continuous pressure increase only above 250°C and reacts exothermically starting at 330°C. In contrast, the electrolyte solution shows a remarkable pressure increase starting at about 170°C, though an onset of an exothermic reaction is observed only near 200°C. This is followed by a sharp temperature increase leading to a thermal runaway.

The basic data presented in Fig. 2 were transformed into plots of self-heating rate (SHR) and pressure development rate (DPR) vs.

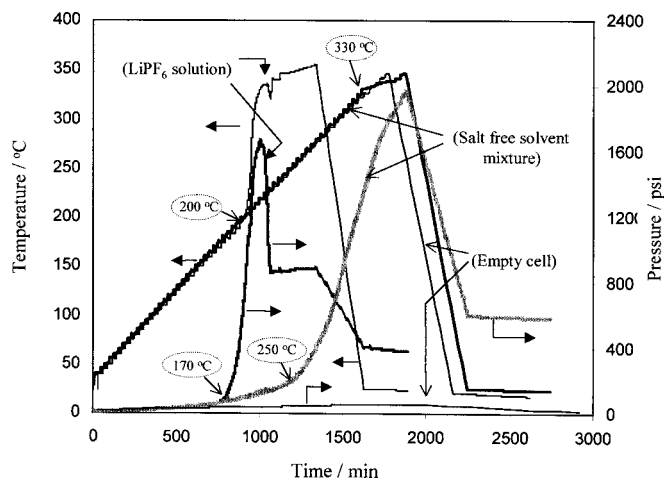


Figure 2. Real time plots of temperature and pressure vs. time (min) from ARC data for empty (air) test cell, solvent mixtures (without salt) of EC:D-EC:DMC (2:1:2 v/v/v) and 1 M LiPF_6 -EC:DEC:DMC (2:1:2 v/v/v) solutions as indicated. The heating rate was 2°C/min (see Experimental section in the text for the full heating program).

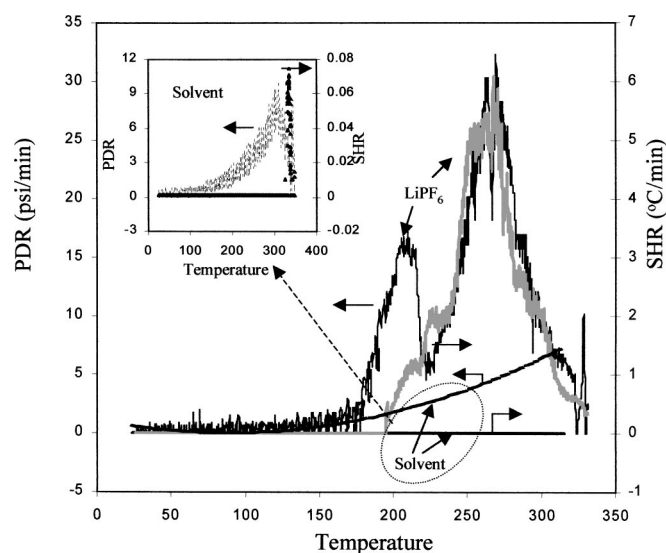


Figure 3. Calculated self-heating rate (SHR) and pressure development rate (PDR) from ARC data for solvent mixtures of EC:DEC:DMC (2:1:2 v/v/v) and 1 M LiPF₆-EC:DEC:DMC (2:1:2 v/v/v) solutions as indicated.

temperature, and are shown in this manner in Fig. 3. This presentation further emphasizes the fact that for the salt-free solvent (see inset) the gas-producing reaction responsible for the increasing PDR beginning at $\sim 170^\circ\text{C}$ is either thermoneutral or endothermic. An exothermic reaction, evidenced by increasing SHR, but not resulting in increased pressure, becomes dominant only after the former reaction has well passed its peak ($\approx 330^\circ\text{C}$). Similarly, a comparison of the PDR and SHR plots for the electrolyte solution (Fig. 3) underlines the conclusion that the gas-producing reaction responsible for the dramatic rise in pressure and in PDR (onset temperature $\approx 170^\circ\text{C}$; local maximum PDR ≈ 17 psi) is either thermoneutral or endothermic. The first part of the PDR peak is not accompanied by a rise in SHR. In view of the difference in sensitivity and the overall heating rate of the two techniques it may be assumed that this first reaction detected by ARC corresponds to the endothermic reaction detected by DSC in the $203\text{--}220^\circ\text{C}$ range (Fig. 1). Returning to the ARC results for the electrolyte solution, it should be noted that the temperature range of the first PDR peak ($170\text{--}225^\circ\text{C}$; maximum PDR ≈ 17 psi min^{-1} at 210°C , Fig. 3) also spans much of the range of the first exothermic reaction shown by the SHR curve (the resolved part of SHR curve is *ca.* $196\text{--}220^\circ\text{C}$). It is therefore possible, though not established, that this reaction also produces some gas. The SHR curve shows a shoulder in the range $\sim 220\text{--}234^\circ\text{C}$ indicating the existence of a second exothermic process. This range corresponds in large part to a trough between two PDR peaks, and there is therefore no clear evidence as to its involving gas evolution.

The temperature range (*ca.* $225\text{--}325^\circ\text{C}$) of the second and major PDR peak, (maximum PDR 32 psi min^{-1} at *ca.* 265°C) nicely overlaps that of the SHR peak of the third and major exothermic reaction (*ca.* $240\text{--}285^\circ\text{C}$; maximum SHR $5.4^\circ\text{C min}^{-1}$) (Fig. 3). This appears therefore to be the source of gas evolution in this range. The multiple steps in the SHR curve at temperatures above 285°C speak for the existence of a number of overlapping processes.

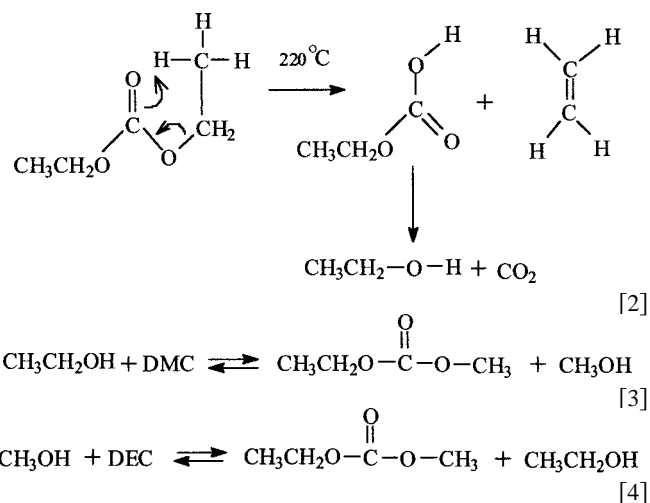
Table I lists the heats of reaction of the LiPF₆ solution for the various exothermic steps, as derived from ARC. Also listed is the data from DSC. The similar values (*ca.* 460 J/g) for the total heat of reaction as obtained by the two methods should be noted.

In order to clarify the nature of the thermal reactions reported above, the solvent (EC:DEC:DMC 2:1:2 v/v/v) and the electrolyte solution were heat-treated in the ARC apparatus, and the heating was stopped at different stages. NMR determinations on solvent samples after heating showed that the solvent mixture is stable up to

Table I. Heat of reactions H_R (J/g) calculated from DSC and ARC data for the solvents mixture and the LiPF₆ solution.

Method	Sample	Heat of reaction, H_R (J/g)		
		Endotherm	Exotherm	Total
DSC	LiPF ₆ solution	37.6 (203-220°C)	-395.7 (220-246°C) -100.0 (250-310°C)	-458.0
ARC	Solvent mixture	—	-22.0 (331-338°C)	-22.0
	LiPF ₆ solution	—	-66.0 (196-218°C) -62.0 (218-235°C) -128.0 (235-282°C) -26.0 (282-291°C) -73.0 (291-316°C) -54.0 (316-334°C) -60.0 (334-350°C)	-467.0

200°C . Heating by the ARC program to 220°C leads to transesterification²² of dimethyl and diethyl carbonates yielding methyl ethyl carbonate. By this temperature 57% of DEC and 50% of DMC had reacted. The excess of 7% in DEC decomposition shows that the DEC is thermally less stable than DMC or EC.¹² Under said conditions DEC had presumably started to undergo Chugaev-type monomolecular elimination (Eq. 2),²³ not possible for EC and DMC. The ethanol thus released initiates an ester interchange cascade with DMC (Eq. 3 and 4). It is also clear from these measurements that at 220°C EC is more stable than both DMC and DEC even to ester interchange since it was found to be unaffected



NMR spectra of solvent mixtures heated by ARC program to 240°C revealed the presence of significant quantities of new products part of which relate to an EC ring opening. At 350°C the solvents were all completely decomposed and polymeric species had formed.

NMR measurements on LiPF₆ solutions after different stages of the thermal reactions revealed that up to 140°C the solutions are stable. The presence of LiPF₆ salt in the solvent mixture lowers the transesterification temperature by 40°C to 180°C (compared to 220°C for the salt-free solvent mixture). Solutions heated to 180°C showed new broad ³¹P peaks (corresponding to 25% of the total P content of the sample) centered at -15 ppm. These are probably due to the formation of polymeric species, which were not identified. In the ¹⁹F spectra of the solution new peaks are also detected. A distinctive singlet at -191 ppm indicates ionic fluoride and a triple quartet at centered -212 ppm is assigned to CH₃CH₂F. Heating up to 220°C leads to pronounced changes. First, the original solvents are completely decomposed, and the ¹H spectra is dominated by a singlet at $\delta 3.63$ assignable to ethylene glycol and a broad peak cen-

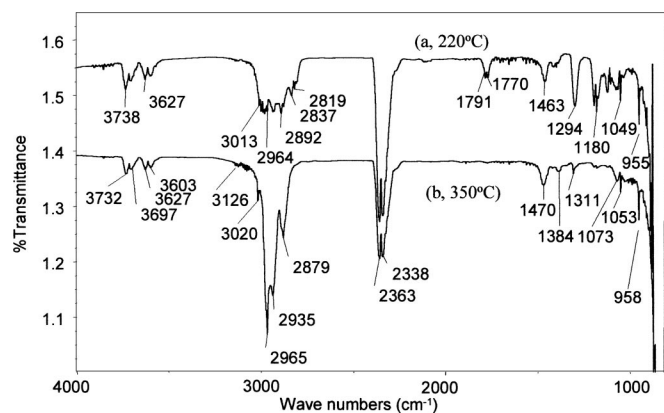


Figure 4. FTIR spectra of gas collected after 1 M LiPF₆-EC:DEC:DMC (2:1:2 v/v/v) solutions heated at 350°C in ARC.

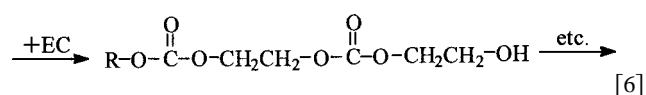
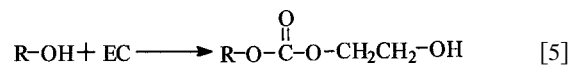
tered at 9 ppm due to the formation of water (H₃O⁺). The PF₆⁻ peak as well as any related P-F absorption are absent in the ¹⁹F spectrum of the liquid phase which is dominated by two broad peaks centered at -144 and -151 ppm belonging to organo-fluorine compounds. The major identified organic fluorinated product is FCH₂CH₂OH (¹⁹F triple triplet centered at -223 ppm; ¹H double triplet centered at 4.50 ppm); smaller amounts of CH₃CH₂F and other FCH₂CH₂X species (triple triplet centered at -226 ppm) are also detected. As may be expected, the ³¹P spectrum shows only a very broad polymer band centered at 6 ppm. Heating up to 350°C leaves no liquid products after cooling.

Analysis of the gas phase after reaction at 220°C shows a quartet (*J* = 46 cps, -268.3 ppm) in the ¹⁹F NMR spectrum attributed to CH₃F, a triple quartet (*J* = 475 cps, -211.7 ppm) corresponding to CH₃CH₂F and a triple triplet centered at -223.4 ppm corresponding to HOCH₂CH₂F. The amount of CH₃CH₂F gas is found to be larger than CH₃F. The ¹H spectrum shows a trace of water (2.15 ppm). The FTIR spectrum (Fig. 4a) of the gas collected from this reaction shows peaks around 3732-3587 cm⁻¹ attributed to ν_{OH}, broad ν_{CH} peaks in the range 3020-2879 cm⁻¹ (organic species), typical peaks around 2363 and 2338 cm⁻¹ attributed to CO₂, typical peaks around 1760-1785 cm⁻¹ attributed to ethylene carbonate, peaks around 1460-1047 cm⁻¹ attributed to δ_{C-H} of CH₂, CH₃ groups and possibly skeletal vibrations of the organic species,²⁴ and a pronounced peak around 830 cm⁻¹ attributed to ν_{P-F} bonds of residual PF₅ in the gas phase. Other less prominent peaks are also present. The organic species thus detected probably included ethylene and X-CH₂CH₂Y (Y = OH, F etc).²⁵

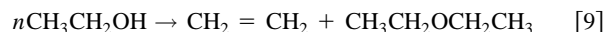
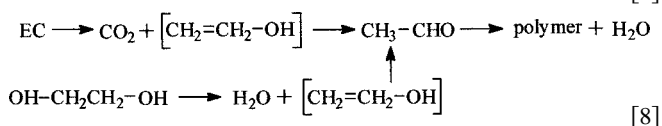
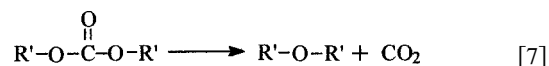
If, after removal of the gaseous products at 220°C, the reaction is allowed to proceed to 350°C, the newly collected gas also shows the presence of CH₃F, CH₃CH₂F, and FCH₂CH₂OH, the latter having become the dominant fluorinated product. If, however, the solution is heated directly to 350°C without the intermediate gas bleeding off at 220°C, only CH₃F and CH₃CH₂F are detected, the former being the dominant product. The fate of FCH₂CH₂OH is unclear (dehydrated? or polymerized?). ¹H spectra show a large amount of water (2.15 ppm) in addition to other broad lines. The FTIR spectrum (Fig. 4b) of the gas collected from that heated directly to 350°C also shows the peaks attributed to ν_{OH}, ν_{CH}, organic species, CO₂, and δ_{C-H} of CH₂, CH₃ groups,²⁴ and a pronounced peak around 830 cm⁻¹ attributed to ν_{P-F} bonds of residual PF₅ in the gas phase. Again, other less prominent peaks were also present. An ethylene carbonate peak is no longer present. The ³¹P spectrum of the condensed phase shows only a very broad polymer band centered at 6 ppm.

The findings presented above lead to the following conclusions. In the salt-free solvent mixture near 220°C there commences a

Chugaev-type monomolecular elimination of DEC which is endothermic, but gas producing, as detailed above in Eq. 2. This identification of the first thermal reaction, which is endothermic, uniquely with the DEC component of the solvent is deduced above from our finding of its faster loss from the mixture. The ethanol released following the elimination of ethylene from DEC (Eq. 2) transesterifies DMC to EMC plus methanol (Eq. 3) and the latter continues the chain by transesterifying DEC to EMC plus methanol (Eq. 4). Transesterification of the linear carbonates is an almost thermoneutral reaction. Upon heating to 240°C the kinetically slower, but thermodynamically more favorable transesterification of the cyclic EC by an available alcohol (CH₃OH, CH₃CH₂OH, or -CH₂CH₂OH) sets in Eq. 5. This ring-opening reaction is exergonic, and it also facilitates the formation of polymer, Eq. 6

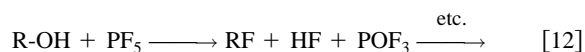
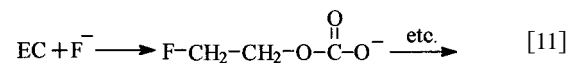
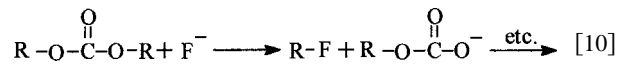


As the temperature is raised to 350°C the reactions of the types illustrated in Eq. 2-6 continue to run their course and are joined by additional thermal decompositions of all the carbonate esters and dehydration of the alcohols along pathways such as



In the electrolyte solutions, the dissociation of LiPF₆ noted in Eq. 1 produces a strong Lewis acid, PF₅ (in addition to the lithium cation) and fluoride ion, which in a hot aprotic medium is both a strong base and a reactive nucleophile. Reactions 1-9 above enjoy acid-base catalysis and their respective onset temperatures are lowered. Again, we attribute the pressure-producing endothermic reaction (onset at ~170°C) specifically to the (catalyzed) decomposition of DEC, similar to Eq. 2 and 3. This assignment is supported by the DSC findings of Kawamura *et al.* that DEC-containing a LiPF₆ electrolyte solution decomposed some 15-20°C lower than the DMC-containing solution.¹² Furthermore, although Botte *et al.* did not explicitly refer to it, the DSC curves they present show an endothermic process as the first thermal reaction only in the case of the electrolyte solutions in which the carbonate ester carries an ethyl group.¹³

In addition, the fluoride ion carries out nucleophilic displacements on the alkyl groups of the carbonate esters, and the PF₅ (and its derivatives) react with alcohols produced (or, at elevated temperatures with the esters). These reactions produce the organic fluoride compounds found (Eq. 10-12)



Conclusions

Studies of the thermal behavior of the commonly used EC-DMC-DEC/LiPF₆ solutions by ARC and DSC, detected one endothermic reaction starting about 170°C, followed by several exothermic reactions in the temperature range 200-325°C. The thermal

decomposition of these solutions involves dissociation of LiPF_6 to PF_5 and fluoride ion, a strong Lewis acid and a reactive nucleophilic base, respectively. The endothermic process detected by the DSC measurements and by the pressure data from the ARC studies involves the reaction of DEC. NMR measurements on LiPF_6 solutions after different stages of thermal reaction revealed that the solutions are stable up to 140°C and upon heating to 180°C undergo an elimination reaction of DEC and followed by transesterification. Further heating leads, by stages to complete decomposition. The major reaction products detected in the condensed and gas phases were $\text{CH}_3\text{CH}_2\text{F}$, CH_3F , $\text{FCH}_2\text{CH}_2\text{Y}$ ($\text{Y} = \text{OH}$, F , etc.), H_2O , and polymer. Most of the exothermic reactions detected involve gas evolution and a build up of excess pressure as a result of the formation of HF , PF_5 , CO_2 , and H_2O and organic species ethylene and alkyl fluorides. Because the presence of DEC as a component of the solvent lowers the onset temperature of decomposition of the electrolyte solution, the advantage of its use must be weighed against its drawbacks for each particular application.

Acknowledgments

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