

Elementary Decomposition Mechanisms of Lithium Hexafluorophosphate in Battery Electrolytes and Interphases

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Abstract

Electrolyte decomposition constitutes an outstanding challenge to long-life Li-ion batteries (LIBs) as well as emergent energy storage technologies, contributing to protection via solid electrolyte interphase (SEI) formation and irreversible capacity loss over a battery's life. Major strides have been made to understand the breakdown of

common LIB solvents; however, salt decomposition mechanisms remain elusive. In this work, we use density functional theory to identify the decomposition of lithium hexafluorophosphate (LiPF_6) salt under SEI formation conditions. Our results suggest that LiPF_6 forms POF_3 primarily through rapid chemical reactions with Li_2CO_3 , while hydrolysis should be kinetically limited at moderate temperatures. We further find that the proposed autocatalysis of POF_3 is selective and that POF_3 preferentially reacts with highly charged oxyanions. These results indicate a means of interphase design in LIBs, suggesting that LiPF_6 reactivity may be controlled by varying the abundance or distribution of inorganic carbonate species or by limiting the transport of PF_6^- through the SEI.

Lithium-ion batteries (LIBs) have in recent years become a cornerstone energy storage technology,¹ powering not just personal electronics but also a growing number of electric vehicles. To continue this trend of electrification in transportation and other sectors, LIBs with higher energy density²⁻⁵ and longer cycle and calendar life⁶ are needed, motivating research into novel battery materials. Battery electrolytes, which are typically the limiting factor in terms of LIB potential window and irreversible capacity loss,⁷⁻⁹ are an especially attractive target for research and development to expand the utility of LIBs. In today's commercial LIBs, the most common electrolytes are comprised of lithium hexafluorophosphate (LiPF_6) dissolved in blends of cyclic carbonates, especially ethylene carbonate (EC), and linear carbonates such as ethyl methyl carbonate.¹⁰⁻¹⁴ Carbonate/ LiPF_6 electrolytes have many desirable properties, including weak ion association and high Li^+ conductivity,¹⁵⁻¹⁷ but they are reactive at low potentials. When paired with graphite negative electrodes, carbonate/ LiPF_6 electrolytes decompose to form a relatively stable passivation film known as the solid electrolyte interphase (SEI),¹⁸⁻²³ which prevents continual electrolyte degradation while allowing reversible charging and discharging. On the other hand, conventional electrolytes based on EC and LiPF_6 are essentially incompatible with high-energy density negative electrodes (e.g. Li metal,^{24,25} Si^{26,27}) and form unstable SEIs, resulting in compar-

atively poor cycle and calendar life.^{28,29}

Due to the significance of the SEI in preserving battery capacity, SEI formation from carbonate/LiPF₆ electrolytes has been extensively studied for decades.³⁰⁻³² Such studies have sought to reveal the fundamental processes involved in the exemplar carbonate/LiPF₆ system and to identify opportunities for improvement through electrolyte engineering. An understanding of the decomposition of carbonate solvents, particularly EC, has been developed through both experiment and theory. In addition to characterizing a wide range of decomposition products - including gases,^{33,34} short-chain organic molecules, oligomers/polymers, and inorganic carbonates (e.g. Li₂CO₃) and oxides (e.g. Li₂O)¹⁹ - plausible elementary mechanisms for EC decomposition have been identified using density functional theory (DFT),³⁵⁻³⁷ *ab initio* molecular dynamics (AIMD),³⁸⁻⁴⁰ and chemical reaction network analysis.⁴¹⁻⁴⁴



In comparison, there are many open questions concerning the decomposition of LiPF₆. It is widely accepted that LiPF₆ decomposes to form LiF, which precipitates and contributes to the SEI.^{30,31,45,46} A range of other products, including POF₃,⁴⁷ difluorophosphoric acid (PF₂OOH),⁴⁸ and some organophosphorus compounds⁴⁹ have been identified by experimental spectroscopy. Moreover, LiPF₆ demonstrates thermal instability,^{50,51} and it has long been suggested that an autocatalytic decomposition mechanism involving POF₃ (Equations 1-2) is responsible.⁵² However, mechanistic explanations for LiPF₆ decomposition remain lacking. Most commonly, hydrolysis^{7,45,46,51,53} is invoked to explain observed PF₆⁻ decomposition (Equations 3-4 show an example mechanism). LiPF₆ has been shown to be unstable in the presence of water,¹⁴ yet hydrolysis alone is insufficient to explain the significant role of LiPF₆ in SEI formation. The DFT study of Okamoto⁵⁴ suggests that PF₆⁻ hydrolysis should

be extremely slow, in agreement with longstanding experimental evidence.⁵⁵ Moreover, LIB electrolytes used in laboratory studies are often rigorously dried, allowing ~ 10 ppm H_2O . Though exposure to high potentials on the positive electrode can both enable the formation of H_2O by reactions with EC⁵⁶ and accelerate PF_6^- hydrolysis,⁵⁷ this cannot explain LiF formation or further LiPF_6 decomposition during early SEI formation before high potentials have been reached or in batteries without high-voltage positive electrodes.



In this work, we explore the decomposition mechanisms of LiPF_6 using DFT at a high level of theory (see Supporting Information for details). We find that water is not necessary to explain the formation of LiF or POF_3 , but rather that PF_5 can react rapidly with readily available Li_2CO_3 during early SEI formation. This mechanism is entirely chemical in nature; it does not depend on electrochemical reduction or oxidation of LiPF_6 and can occur at any depth of the SEI as long as the transport of PF_6^- to inorganic carbonate domains is feasible. Hence, porosity, morphology and transport properties of the SEI also becomes a relevant factor. We then study POF_3 autocatalysis, using PF_2OOH and LiPF_2O_2 as model intermediates. Due to selective reactivity between POF_3 and highly charged oxyanions, LiPF_2O_2 is preferred over PF_2OOH in the absence of an oxidizing potential. Our calculations additionally indicate that overall, the POF_3 autocatalytic cycle is limited by a slow intramolecular fluorine transfer step. These findings answer longstanding questions regarding the reactivity of LiPF_6 and suggest new routes for controlling salt reactivity during SEI formation.

Decomposition of LiPF_6 to POF_3 : We begin by considering the formation of PF_5 , which is a key intermediate in essentially all LiPF_6 reaction routes considered in the literature and in this work. We find that the elimination of LiF from LiPF_6 to form PF_5 (Equation

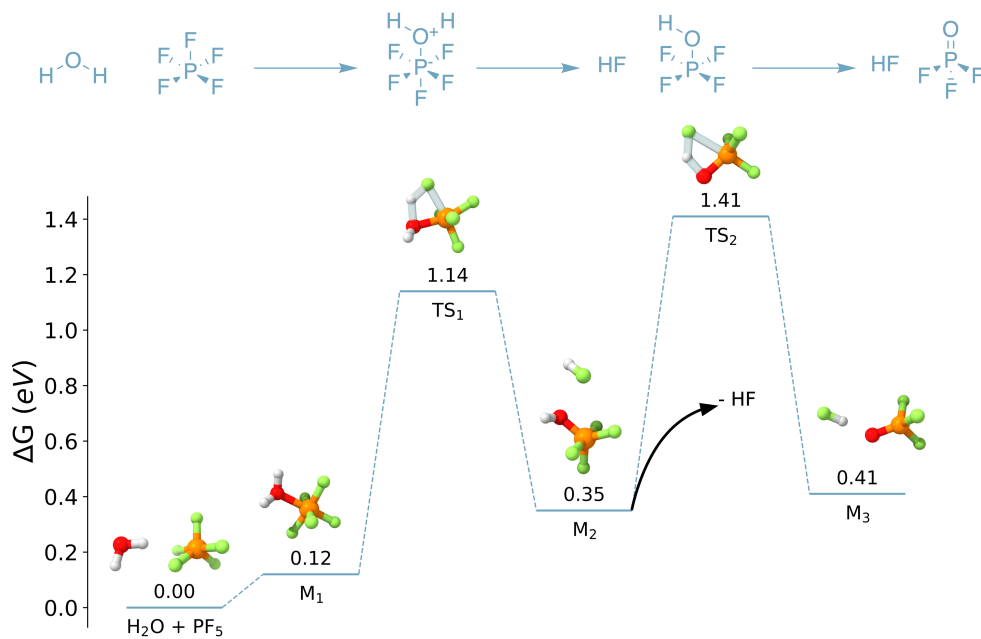


Figure 1: Hydrolysis of PF_5 to form PO_2F_2 and 2HF . This mechanism is overall thermodynamically unfavorable and involves two reactions with high barriers ($\Delta G^\ddagger > 1.00$ eV).

3) has no transition-state but is endergonic, with $\Delta G = 1.04$ eV. However, we note that the product in this reaction is a solution-phase molecule of LiF , whereas we expect that LiF will precipitate, forming solid deposits within the SEI. This reaction is more likely to occur when considering the possibility that LiF could be stabilized by precipitation. Okamoto⁵⁴ previously found that the deposition of solid LiF ($\text{LiF}(\text{solv}) \longrightarrow \text{LiF}(\text{solid})$) has $\Delta G = -1.17$ eV, which would make Equation 3 overall exergonic. More recently, Cao et al.⁵⁸ used DFT and AIMD to show that LiPF_6 decomposition by either chemical or electrochemical means is greatly accelerated in the presence of existing LiF . Here, we report the reaction energies and energy barriers of LiF elimination reactions like Equation 3 without including the effect of a surface or LiF precipitation. However, we emphasize that we expect these reactions, in general, to be more favorable than what is predicted based on calculations with molecular LiF in solution.

Even once PF_5 is formed, Figure 1 confirms that, at our chosen level of theory, the direct hydrolysis of PF_5 by H_2O is unfavorable. Each of the three hydrolysis steps - the addition

of H_2O to PF_5 ($\text{H}_2\text{O} + \text{PF}_5 \longrightarrow \text{M}_1$), the elimination of HF to form PF_4OH ($\text{M}_1 \longrightarrow \text{M}_2$), and the elimination of HF from PF_4OH ($\text{M}_2 \longrightarrow \text{M}_3$) - is predicted to be endergonic. Further, the latter two steps both have energy barriers $\Delta G^\ddagger > 1.00$ eV, agreeing with the experimental observation that hydrolysis is slow at room temperature. Significant thermal activation beyond temperatures reached in normal LIB cycling conditions would be required to enable LiPF_6 hydrolysis.

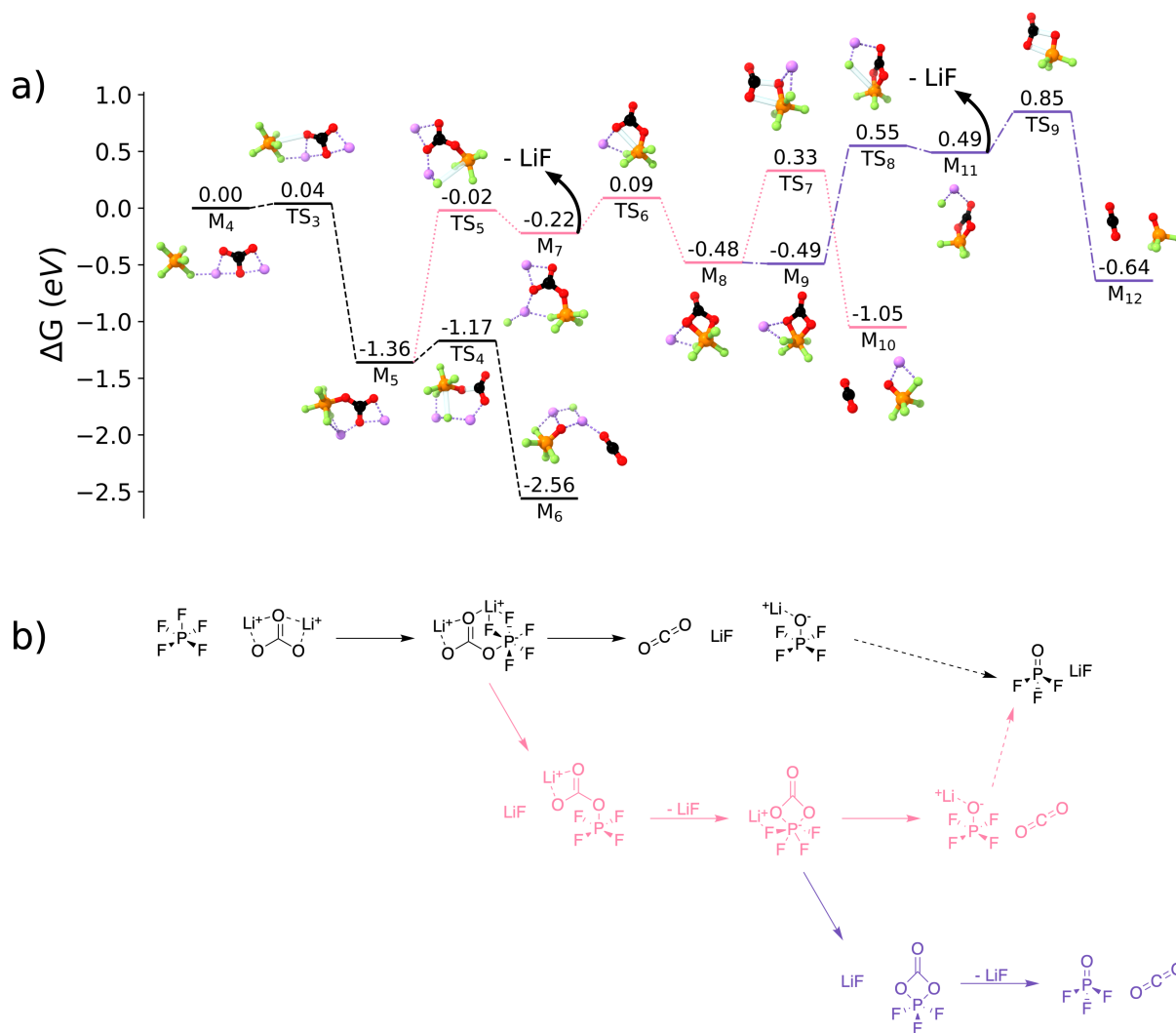


Figure 2: Energy diagram (a) and scheme (b) for the reaction between PF_5 and Li_2CO_3 to form 2LiF , CO_2 , and POF_3 . In the black and pink paths, LiPOF_4 is formed (M_6 , M_{10}). LiPOF_4 can decompose to form LiF and POF_3 with $\Delta G^\ddagger = 0.63$ eV, $\Delta G = 0.28$ eV, but this is not shown in (a) (see Supporting Information).

An alternate mechanism involves the reaction of PF_5 with Li_2CO_3 (Figure 2). Reactions

between PF_5 and inorganic carbonates have been proposed in the past^{59,60} on the basis of the observed evolution of CO_2 and POF_3 upon mixing of LiPF_6 and Li_2CO_3 , but this route has largely been neglected in favor of hydrolytic mechanisms. Moreover, to the best of our knowledge, this mechanism has never been studied by first-principles calculations.

We find that PF_5 reacts vigorously with Li_2CO_3 . An initial addition step between the two reactants ($\text{M}_4 \longrightarrow \text{M}_5$) has a low barrier of $\Delta G^\ddagger = 0.04$ eV. The adduct (M_5) then dissociates in a single concerted reaction, yielding LiF , CO_2 , and LiPOF_4 with $\Delta G^\ddagger = 0.20$ eV. Finally, to form POF_3 , LiPOF_4 eliminates an additional molecule of LiF , with $\Delta G^\ddagger = 0.63$ eV, $\Delta G = 0.28$ eV (not shown in Figure 2; see Supporting Information). We again note that we expect both ΔG and ΔG^\ddagger for LiF elimination reactions to be lowered if precipitation of LiF on a surface is allowed. Even without any corrections for the instability of molecular LiF produced in $\text{M}_5 \longrightarrow \text{M}_6$ and $\text{LiPOF}_4 \longrightarrow \text{LiF} + \text{POF}_3$, this mechanism represents one of the most thermodynamically and kinetically favorable elementary mechanism for PF_5 decomposition yet reported.

If it does not dissociate completely, the adduct M_5 may instead eliminate LiF ($\text{M}_5 \longrightarrow \text{M}_7$), though this reaction suffers from a high predicted barrier of $\Delta G^\ddagger = 1.34$ eV. After LiF elimination, an additional oxygen from the carbonate group binds to phosphorus to form a ring complex M_8 . By eliminating CO_2 , either immediately ($\text{M}_8 \longrightarrow \text{M}_{10}$, $\Delta G^\ddagger = 0.81$ eV) or following the elimination of another LiF ($\text{M}_{11} \longrightarrow \text{M}_{12}$, $\Delta G^\ddagger = 0.36$ eV), this ring complex also forms LiPOF_4 (M_{10}) or POF_3 (M_{12}).

The proposed mechanisms shown in Figure 2 rely only on Li_2CO_3 , which should be abundant at the negative electrode, especially during early SEI formation.^{21,31,38,60-62} The reaction of PF_5 and Li_2CO_3 is also entirely chemical in nature; none of the reactions in Figure 2 depend on electrochemical oxidation or reduction. As a result, the decomposition should not depend explicitly on applied potential, the proximity to the anode surface, or the availability of electrons. Therefore, we predict that the decomposition of PF_5 can occur anywhere in the SEI, so long as inorganic carbonates like Li_2CO_3 are present. This being

said, because Li_2CO_3 is formed in the SEI as a result of electrochemical reduction of EC,^{38,44} the overall rate of POF_3 formation via the reaction of PF_5 with Li_2CO_3 will implicitly have a potential dependence.

While our focus in this work is on LiPF_6 decomposition during SEI formation, it is worth noting that Li_2CO_3 is an impurity formed during the synthesis of common transition metal oxide positive electrodes.⁵⁹ Accordingly, the mechanisms described in Figure 2 could occur at the positive electrode as well as at the negative electrode or the SEI.

Autocatalytic decomposition of PF_5 : Figure 2 indicates that POF_3 emerges rapidly by reaction with Li_2CO_3 during SEI formation. This hints that the proposed autocatalytic mechanisms for POF_3 (re)formation (Equations 1-2), which rely on POF_3 and carbonate species, are chemically plausible.

To confirm the mechanism of POF_3 autocatalysis at elevated temperature, we first consider the formation of $\text{PF}_2\text{O}_2\text{R}$ species (Figure 3). Specifically, we explore the formation of PF_2OOH from H_2CO_3 (Figure 3a) and LiHCO_3 (Figure 3b) and the formation of LiPF_2O_2 by Li_2CO_3 (Figure 3c). In addition to their relevance for POF_3 formation and LiPF_6 decomposition, $\text{PF}_2\text{O}_2\text{R}$ species and in particular difluorophosphoric acid (PF_2OOH) have been blamed as major contributors to the decomposition of SEI species and the loss of battery capacity.^{63,64} Jayawardana et al. have argued that PF_2OOH should form at the positive electrode, as a result of PF_6^- oxidation.⁶³ If PF_2OOH and related species could form at the negative electrode without high potentials, it could have significant implications for the stability of the SEI.

Figure 3a shows a mechanism for a chemical reaction between H_2CO_3 and POF_3 . The initial addition reaction between POF_3 and H_2CO_3 ($\text{H}_2\text{CO}_3 + \text{POF}_3 \longrightarrow \text{M}_{13}$) is thermodynamically unfavorable ($\Delta G = 1.62 \text{ eV}$). Subsequent reactions to form HF, CO_2 , and PF_2OOH do not face significant barriers and should occur rapidly. The reaction between POF_3 and LiHCO_3 (Figure 3b) follows a similar mechanism. The addition step ($\text{M}_{16} \longrightarrow \text{M}_{17}$) is also endergonic ($\Delta G^\ddagger = 0.48 \text{ eV}$, $\Delta G = 0.52 \text{ eV}$), though we suggest that it could be ac-

cessed at moderate temperatures. Addition by LiHCO_3 is followed by the elimination of LiF ($\text{M}_{18} \longrightarrow \text{M}_{19}$), which is analogous to the elimination of HF in Figure 3a, ($\text{M}_{13} \longrightarrow \text{M}_{14}$). Following the complete removal of LiF , M_{19} can undergo the same concerted proton transfer and CO_2 elimination shown in Figure 3a ($\text{M}_{14} \longrightarrow \text{M}_{15}$).

In contrast, POF_3 adds easily to Li_2CO_3 (Figure 3c, $\text{M}_{20} \longrightarrow \text{M}_{21}$), with $\Delta G^\ddagger = 0.15$ eV and $\Delta G = -0.01$ eV. We explain the difference in the thermodynamics of the reactions between POF_3 and H_2CO_3 , LiHCO_3 , and Li_2CO_3 by considering atomic partial charges (Figure 3d). POF_3 is reactive towards the highly anionic oxygens in Li_2CO_3 , but not towards the less charged oxygens in LiHCO_3 and H_2CO_3 . A similar trend is found for the reaction between PF_5 and inorganic carbonates (see Supporting Information). Though PF_2OOH formation via LiHCO_3 is possible, the difficulty of addition with protonated carbonates suggests that, barring electrochemical processes, LiPF_2O_2 should be more abundant at the negative electrode than PF_2OOH . Nonetheless, the prediction that PF_2OOH and LiPF_2O_2 can form at or near the SEI without the need for cross-talk from the positive electrode motivates further efforts to understand the interactions between these species and other SEI components.

Mechanisms for the reformation of POF_3 (completing the autocatalytic cycle in Equation 2) are shown in Figure 4. Following a similar trend to that shown in Figure 3d, the attack of PF_5 by the protonated PF_2OOH (Figure 4a, $\text{PF}_2\text{OOH} + \text{PF}_5 \longrightarrow \text{M}_{25}$) is thermodynamically unfavorable, while LiPF_2O_2 can favorably add to PF_5 (Figure 4b, $\text{LiPF}_2\text{O}_2 + \text{PF}_5 \longrightarrow \text{M}_{28}$). After the initial addition, an intramolecular fluorine transfer is required; for both $\text{PF}_2\text{O}_2\text{R}$ species considered, this step is thermodynamically unfavorable and suffers from a high barrier ($\text{M}_{25} \longrightarrow \text{M}_{26}$, $\Delta G^\ddagger = 0.95$ eV; $\text{M}_{29} \longrightarrow \text{M}_{30}$, $\Delta G^\ddagger = 1.76$ eV). While both intramolecular fluorine transfer reactions are kinetically limited at room temperature (Figure 4 c-d), the reaction without Li^+ can occur rapidly at elevated temperature (especially $T > 150^\circ\text{C}$). After fluorine transfer, the two mechanisms in Figure 4a-b diverge. In Figure 4a, a concerted proton transfer and elimination step occurs ($\text{M}_{26} \longrightarrow \text{M}_{27}$), yielding POF_3 and PF_4OH . PF_4OH

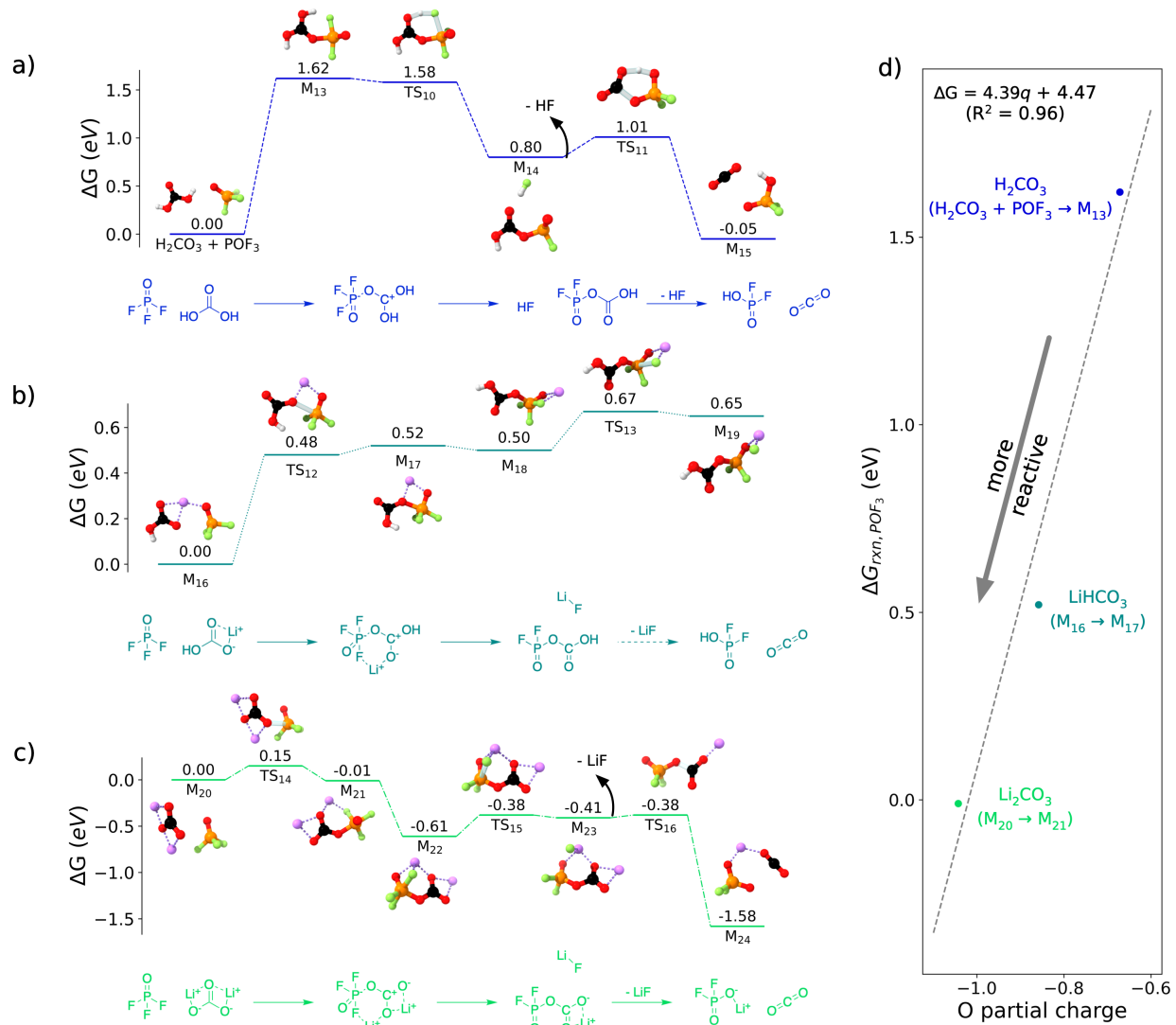


Figure 3: Reactions between POF_3 and simple inorganic carbonates (**a**) H_2CO_3 , **b**) LiHCO_3 , and **c**) Li_2CO_3) to form CO_2 and either PF_2OOH or LiPF_2O_2 . In **b**), the final step to form PF_2OOH from M_{19} is omitted, as it is identical to the final step in **a**) ($\text{M}_{14} \rightarrow \text{M}_{15}$) with the substitution of LiF as the leaving group rather than HF . A trend between the partial charge of the reacting oxygen(s) (see Supporting Information for details) and the reaction energies with POF_3 for each carbonate considered is shown in **d**). A linear fit, $\Delta G = 4.39q + 4.47$, where q = the most negative oxygen partial charge, shows strong agreement ($R^2 = 0.96$) within the family of inorganic carbonates.

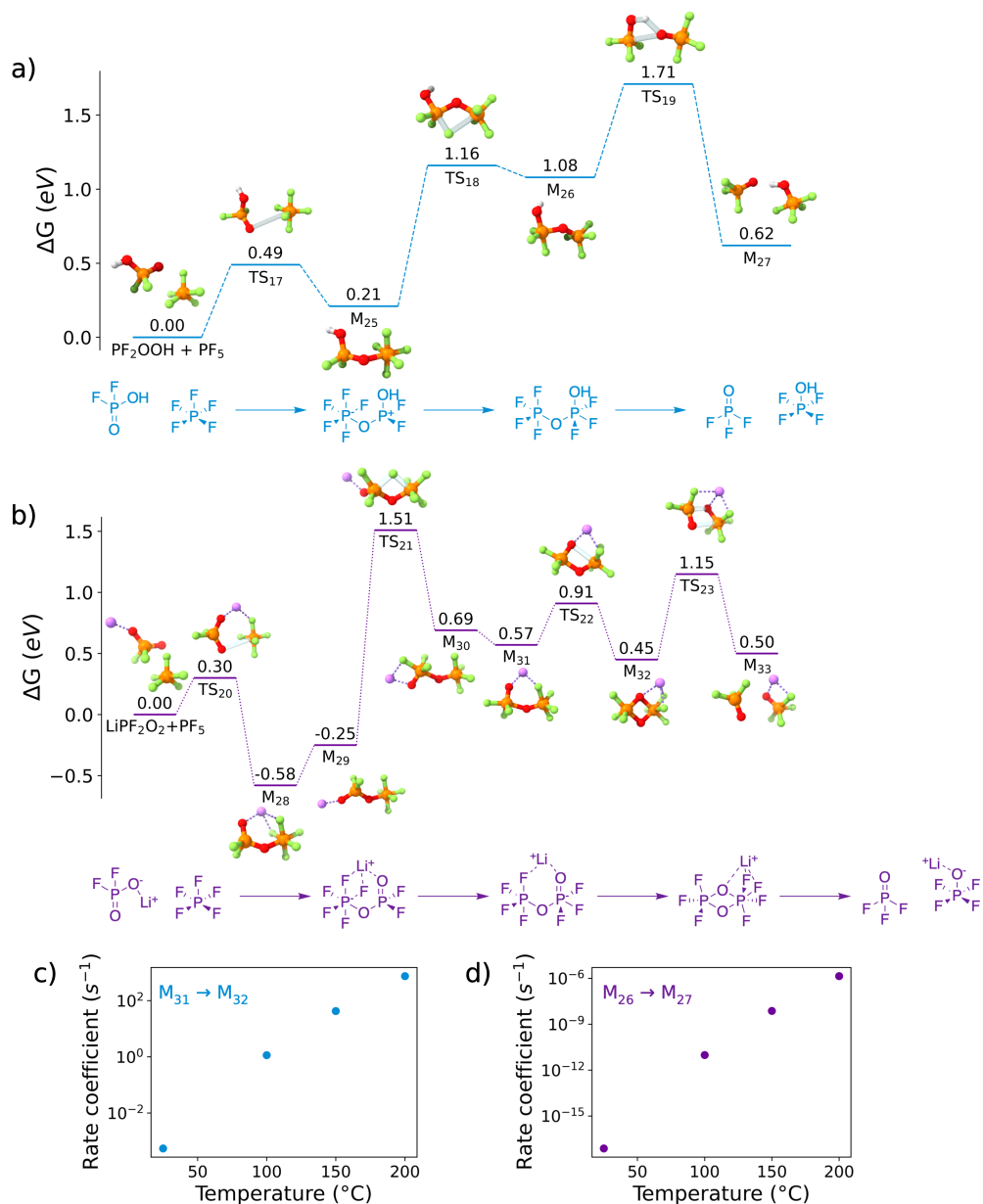


Figure 4: Possible routes for the reformation of POF_3 from PF_2OOH (a) and LiPF_2O_2 (b). Both mechanisms are kinetically limited due to an extremely unfavorable intramolecular fluorine transfer step ($\text{M}_{25} \rightarrow \text{M}_{26}$, $\text{M}_{29} \rightarrow \text{M}_{30}$), which makes POF_3 autocatalysis unlikely at modest temperatures. Rate coefficients for the fluorine transfer step are provided in c) for the PF_2OOH pathway and in d) for the LiPF_2O_2 pathway.

can subsequently eliminate HF to form POF_3 , as shown in Figure 1. In Figure 4b, a four-member O-P-O-P ring is formed ($\text{M}_{31} \longrightarrow \text{M}_{32}$) and POF_3 is eliminated ($\text{M}_{32} \longrightarrow \text{M}_{33}$), leaving LiPOF_4 which could then form LiF and POF_3 as previously discussed.

Our mechanism confirms the previously reported autocatalytic formation of POF_3 . We find, in agreement with earlier experimental studies,^{50,52} that this cycle requires significant thermal activation ($T \sim 150^\circ\text{C}$). This is primarily due to a sluggish intramolecular fluorine transfer and, specifically for the mechanism requiring PF_2OOH as an intermediate, the high barrier for HF elimination to reform POF_3 . While we have found a mechanism for POF_3 autocatalysis that does not require any water, the significantly lower barrier for the pathway involving PF_2OOH indicates that LiPF_6 thermal decomposition could be initiated and accelerated by LiPF_6 hydrolysis,⁴⁷ which is accessible at elevated temperature.

Conclusions: LiPF_6 is an exceptional salt that is likely to play a major role in the LIB market for years to come. While some decomposition of LiPF_6 is desirable to form a functional SEI, continued breakdown can severely limit the life of LiBs. In this work, we identified a facile elementary decomposition mechanism of LiPF_6 using first-principles DFT simulations. Our results imply that under normal battery cycling conditions, the major decomposition mechanism of LiPF_6 does not depend on water or on electrochemical salt reduction. Rather, LiPF_6 forms the expected products LiF, POF_3 , LiPF_2O_2 , and potentially PF_2OOH via entirely chemical reactions with inorganic carbonates (especially Li_2CO_3). PF_5 and POF_3 show a strong affinity for highly charged oxyanions, suggesting that that efforts to control the reactivity of LiPF_6 should focus on limiting the exposure of PF_5 to oxyanion species, including and especially inorganic carbonates like Li_2CO_3 , in the SEI as well as on the surface of positive electrodes. This consideration may include morphological control, such as reducing porosity and/or abundance of inorganic species in the outer regions of the SEI. Identification of the primary PF_6 breakdown mechanism will also enable future work including studies of the elementary reaction mechanisms between LiPF_6 decomposition products (especially $\text{PF}_2\text{O}_2\text{R}$ species) and other SEI species (e.g. organic carbonates) as well

as the formation mechanisms of organophosphorus compounds and phosphate polymers in the SEI.

Author Contributions

Conceptualization: E.W.C.S.-S., K.A.P.; Formal analysis: E.W.C.S.-S., T.B.P., H.D.P.; Funding acquisition: E.W.C.S.-S., H.D.P., S.M.B., K.A.P.; Investigation: E.W.C.S.-S., T.B.P., H.D.P.; Resources: K.A.P.; Supervision: E.W.C.S.-S., K.A.P.; Visualization: E.W.C.S.-S.; Writing - original draft: E.W.C.S.-S., T.B.P.; Writing - review & editing: all authors.

Competing Interests Statement

The authors declare no competing financial interests.

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Supporting Information Available

Structural and thermochemical data for all molecules considered in this study; computational methods; discussion of additional reaction mechanisms for LiPF₆ decomposition.

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