

Phase Behavior That Enables Solvent-Free Carbonate-Promoted Furoate Carboxylation

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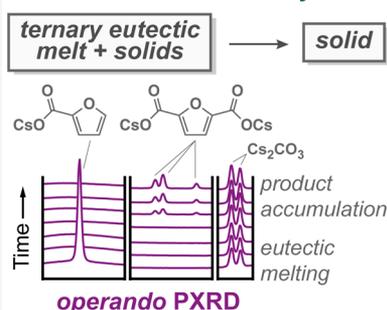
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ABSTRACT: Solvent-free chemistry has been used to streamline synthesis, reduce waste, and access novel reactivity, but the physical nature of the reaction medium in the absence of solvent is often poorly understood. Here we reveal the phase behavior that enables the solvent-free carboxylation reaction in which carbonate, furan-2-carboxylate (furoate), and CO₂ react to form furan-2,5-dicarboxylate (FDCA²⁻). This transformation has no solution-phase analogue and can be applied to convert lignocellulose into performance-advantaged plastics. Using *operando* powder X-ray diffraction and thermal analysis to elucidate the temperature- and conversion-dependent phase composition, we find that the reaction medium is a heterogeneous mixture of a ternary eutectic molten phase, solid Cs₂CO₃, and solid Cs₂FDCA. During the reaction, the amounts of molten phase and solid Cs₂CO₃ diminish as solid Cs₂FDCA accumulates. These insights are critical for increasing the scale of furoate carboxylation and provide a framework for guiding the development of other solvent-free transformations.

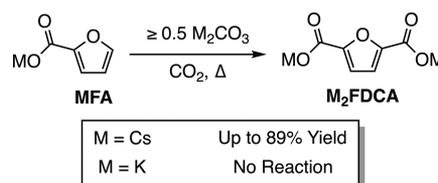
solvent-free C–H carboxylation



Solvent-free reactions have been investigated primarily as a means to improve the practicality of conventional solution-phase reactions by reducing waste, accelerating the rate, or simplifying purification.^{1–9} The unusual properties of a reaction medium composed of neat reactants also raise the possibility of accessing reactivity that is very difficult or impossible to recapitulate in solution. To this end, we recently showed that carbonate (CO₃²⁻) can promote C–H carboxylation of very weakly acidic aryl C–H bonds (pK_a > 35 in organic solvent) in carefully selected solvent-free alkali salts at elevated temperatures.^{10–13} By contrast, even under forcing conditions in organic solvent, CO₃²⁻ has been found to be incapable of promoting carboxylation of C–H bonds with pK_a values of >27.¹⁴ The ability to use a simple, regenerable base such as CO₃²⁻ is essential if carboxylation is to be applied to scalable chemical synthesis. Solvent-free alkali salts unlock this possibility for some targets, but a better understanding of the reaction medium is needed to realize this potential.

A promising application of solvent-free CO₃²⁻-promoted C–H carboxylation is the conversion of furan-2-carboxylate (furoate) into furan-2,5-dicarboxylate (FDCA²⁻) (Scheme 1). The protonated form of the carboxylation product, furan-2,5-dicarboxylic acid (FDCA), is a potential platform chemical for the synthesis of performance-advantaged plastics.^{15,16} Extensive efforts to produce FDCA on a commercial scale from C₆ sugars (glucose and fructose) have been impeded by the technical difficulties and process complexity of dehydrating and oxidizing C₆ sugars.¹⁷ C–H carboxylation opens a new route to FDCA from underutilized C₅ sugar feedstocks (inedible hemicellulose) and avoids many of the process challenges that have plagued C₆ routes.¹¹

Scheme 1. Solvent-Free Carbonate-Promoted Furoate Carboxylation

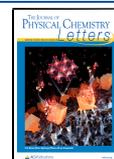


In its simplest form, furoate carboxylation is performed by combining alkali furoate (MFA) with at least 0.5 equiv of alkali carbonate and heating the salt mixture under CO₂. Yields of FDCA²⁻ as high as 89% have been obtained in laboratory-scale experiments (up to >100 g), but the performance shows a strong dependence on the identity of the alkali cation (Scheme 1). When using a single alkali cation, high yields of FDCA²⁻ can be achieved with Cs⁺, but no detectable yield is obtained with any of the other alkali cations. Herein, we present a detailed investigation of the physical and structural properties of the reaction mixture components for solvent-free furoate carboxylation. Using a combination of X-ray diffraction and thermal analysis techniques, we elucidate the phase behavior

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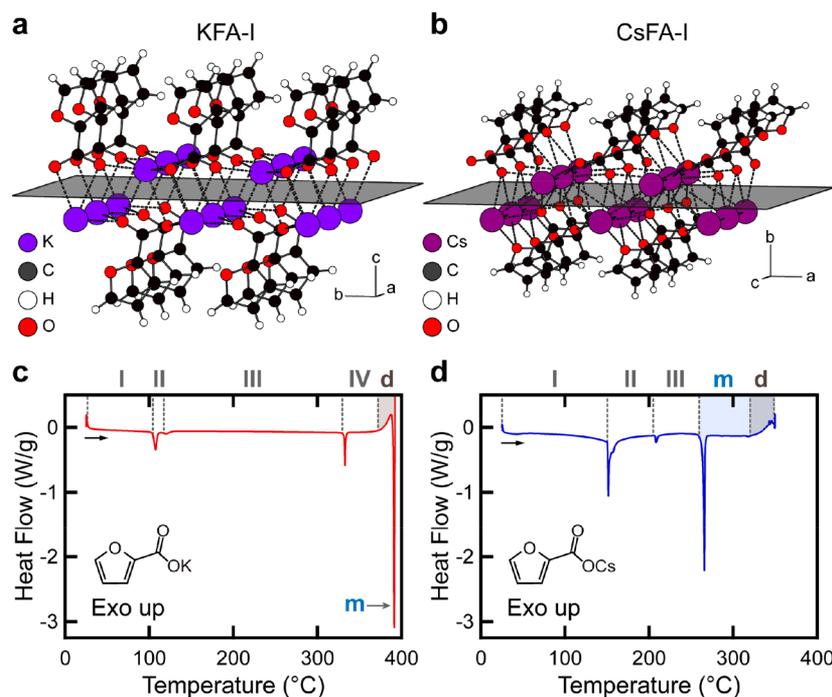


Figure 1. Structural and thermal properties of alkali furoate salts. (a) Layered structure of the ambient-temperature polymorph of potassium furoate (KFA), as determined from refined single-crystal X-ray diffraction data. The (001)-family plane bisecting the cation layer is shown for the sake of clarity. (b) Layered structure of the ambient-temperature polymorph of cesium furoate (CsFA), as determined from synchrotron powder X-ray diffraction data by simulated annealing. The (010)-family plane bisecting the cation layer is shown for the sake of clarity. (c and d) Differential scanning calorimetry heating curves of KFA and CsFA salts, respectively. Temperature regions corresponding to different crystalline polymorphs are labeled above the plots. The region marked “d” corresponds to thermal decomposition, while the peak (or region) marked “m” corresponds to the isotropic melt.

that enables solvent-free furoate carboxylation in Cs^+ salts and explain the lack of reactivity in pure K^+ salts. Our findings reveal how reactivity in this system depends on the phase equilibria that exist within multicomponent salt mixtures.

In the solvent-free furoate carboxylation reaction, the material that makes up the reaction medium consists initially of a mixture of alkali furoate (MFA) and alkali carbonate (M_2CO_3). Alkali carbonates are inorganic crystalline solids with high melting points ($T_m = 899\text{ }^\circ\text{C}$ for $\text{M} = \text{K}$; $T_m = 793\text{ }^\circ\text{C}$ for $\text{M} = \text{Cs}$).¹⁸ Hence, any phase behavior that occurs in the mixture at carboxylation temperatures ($<280\text{ }^\circ\text{C}$) can be expected to derive primarily from the furoate component. To understand the cation dependence of furoate carboxylation reactivity, we looked first to contrast the structural and thermal properties of potassium and cesium furoate.

Both potassium furoate (KFA) and cesium furoate (CsFA) are crystalline solids at room temperature, though CsFA is distinctly more hygroscopic. A single-crystal X-ray structure obtained for KFA shows that the salt packs in the form of two-dimensional sheets of potassium cations sandwiched between organic anion layers (Figure 1a and Figures S1 and S2). In contrast to KFA, diffraction-quality single crystals of CsFA could not be isolated for determination of a crystal structure, a common problem for aromatic carboxylates.¹⁹ However, ambient-temperature synchrotron powder X-ray diffraction (PXRD) patterns of anhydrous CsFA indicate that the salt also possesses a layered structure, evidenced by an intense low-index peak. A plausible room-temperature structure for CsFA was determined from PXRD data by a simulated annealing procedure²⁰ after indexing of ambient-temperature PXRD patterns for anhydrous CsFA collected at two independent

synchrotron beamlines (Figures S3–S5; see the Supporting Information for additional details). The packing in the resulting structure (Figure 1b) is very similar to that in KFA.

Given the similarity of potassium and cesium furoate at ambient temperature, any differences in the properties of the two salts that are related to their disparity in carboxylation reactivity must manifest only at elevated temperatures. Thermal analysis reveals that the key difference between KFA and CsFA is that only the latter salt can exist as a stable isotropic melt. As with many other alkali carboxylate salts,^{21–23} alkali furoates were found to exhibit complex polymorphism. Differential scanning calorimetry (DSC) thermograms collected for samples of KFA and CsFA show that upon being heated from room temperature, both salts undergo a series of endothermic events prior to the onset of exothermic decomposition (Figure 1c,d). In both cases, the highest-temperature endothermic transition was identified as melting ($T_m = 390\text{ }^\circ\text{C}$ for $\text{M} = \text{K}$; $T_m = 264\text{ }^\circ\text{C}$ for $\text{M} = \text{Cs}$), while the lower-temperature endothermic events correspond to solid–solid transitions between crystalline or semicrystalline MFA polymorphs (denoted by Roman numerals increasing with temperature from I for the ambient-temperature polymorph). The assignment of these thermal events was further corroborated by thermogravimetric analysis, polarized optical microscopy, and variable-temperature PXRD techniques (Figures S6–S11). Importantly, while the melting transition for KFA overlaps with its region of thermal decomposition, melting of CsFA occurs approximately $65\text{ }^\circ\text{C}$ below the onset of its own decomposition event ($T_d = 328\text{ }^\circ\text{C}$). The ability of CsFA to exist in a molten form is crucial for its ability to participate in solvent-free chemistry.

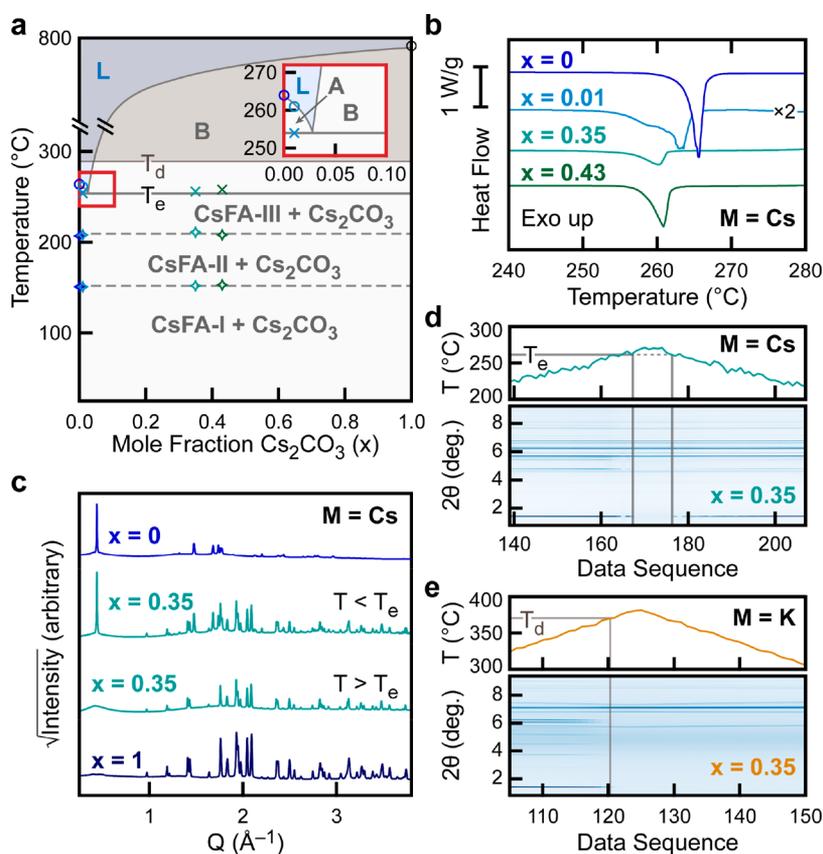


Figure 2. Phase equilibria in binary MFA/ M_2CO_3 mixtures. (a) Phase equilibrium diagram for the CsFA/ Cs_2CO_3 anhydrous system. Marked temperatures of melting transitions (○), eutectic transitions (×), and solid–solid phase transitions (four-pointed star) were determined from DSC measurements. All two-phase regions below the eutectic temperature are labeled with their constituent solid phases. Region L corresponds to the uniform melt. Region A (inset) corresponds to the two-phase mixture of CsFA-III and eutectic melt, and region B corresponds to the two-phase mixture of Cs_2CO_3 and eutectic melt. All regions above the line marked T_d are inaccessible due to decomposition of the CsFA component. (b) DSC thermograms comparing melting of pure CsFA with eutectic melting in CsFA/ Cs_2CO_3 mixtures of varying composition. The $x = 0.01$ trace has been scaled vertically to highlight the two distinct thermal events (eutectic formation and liquidus melting) observed. (c) PXRD patterns comparing a mixture of CsFA and Cs_2CO_3 with $x = 0.35$ before and after its eutectic melting event. Shown for reference are powder patterns for pure CsFA-III ($x = 0$) and pure Cs_2CO_3 ($x = 1$). (d and e) Temperature profiles (top) and PXRD contour plots (bottom) for variable-temperature PXRD ($\lambda = 0.35380$; 5 sccm He gas) performed on a mixture of CsFA and Cs_2CO_3 with $x = 0.35$ and KFA and K_2CO_3 with $x = 0.35$, respectively. The diffraction intensity in the contour plots increases from white to blue. Melting or decomposition events as evidenced by the disappearance of diffraction peaks are marked.

The furoate salt is only one component of the carboxylation reaction medium, however. The stoichiometry of furoate carboxylation promoted by M_2CO_3 requires a minimum of 0.5 molar equivalent of M_2CO_3 relative to MFA to achieve complete conversion to the alkali dicarboxylate salt (M_2FDCA). To understand the physical properties of the reaction mixture at the outset of a solvent-free furoate carboxylation reaction, the impact of the addition of M_2CO_3 on the thermal properties of the MFA salt must be examined.

A combination of thermal analysis and variable-temperature PXRD reveals that CsFA and Cs_2CO_3 constitute a binary eutectic system (Figure 2a). DSC thermograms were collected for a series of mixtures of CsFA and Cs_2CO_3 salts with varying compositions. Increasing the Cs_2CO_3 mole fraction (x) in the mixture affects the position and appearance of the final endothermic transition observed in the DSC heating curve (Figure 2b). When a very small amount of Cs_2CO_3 is present ($x = 0.01$), the transition shifts to a lower temperature relative to the melting transition observed for pure CsFA. The peak also presents with a distinct shoulder, with the onset of this shoulder occurring at 256 °C. For higher values of x , only a

single endothermic event is observed, also with an onset temperature of approximately 256 °C. Variable-temperature PXRD was used to further examine the nature of this transition, using $x = 0.35$ to match the 1:0.55 CsFA: Cs_2CO_3 stoichiometry most commonly employed in the synthetic reaction.¹⁰ Comparison of PXRD patterns collected before and after heating this mixture of CsFA and Cs_2CO_3 past 256 °C shows that the transition corresponds to the selective disappearance of diffraction peaks that can be attributed to solid CsFA-III, while anhydrous crystalline Cs_2CO_3 remains (Figure 2c). Moreover, the transition was shown to be reversible. Immediately cooling the mixture upon disappearance of the CsFA peaks leads to their reappearance as CsFA-III recrystallizes at approximately the same temperature (Figure 2d).

These observations are all consistent with a decrease in the CsFA melting point of ~ 8 °C upon addition of Cs_2CO_3 through formation of a eutectic. For all compositions of relevance to the CsFA carboxylation reaction (i.e., $x \geq 0.33$), the reaction necessarily occurs from a heterogeneous mixture of solid crystalline Cs_2CO_3 and a molten eutectic that contains

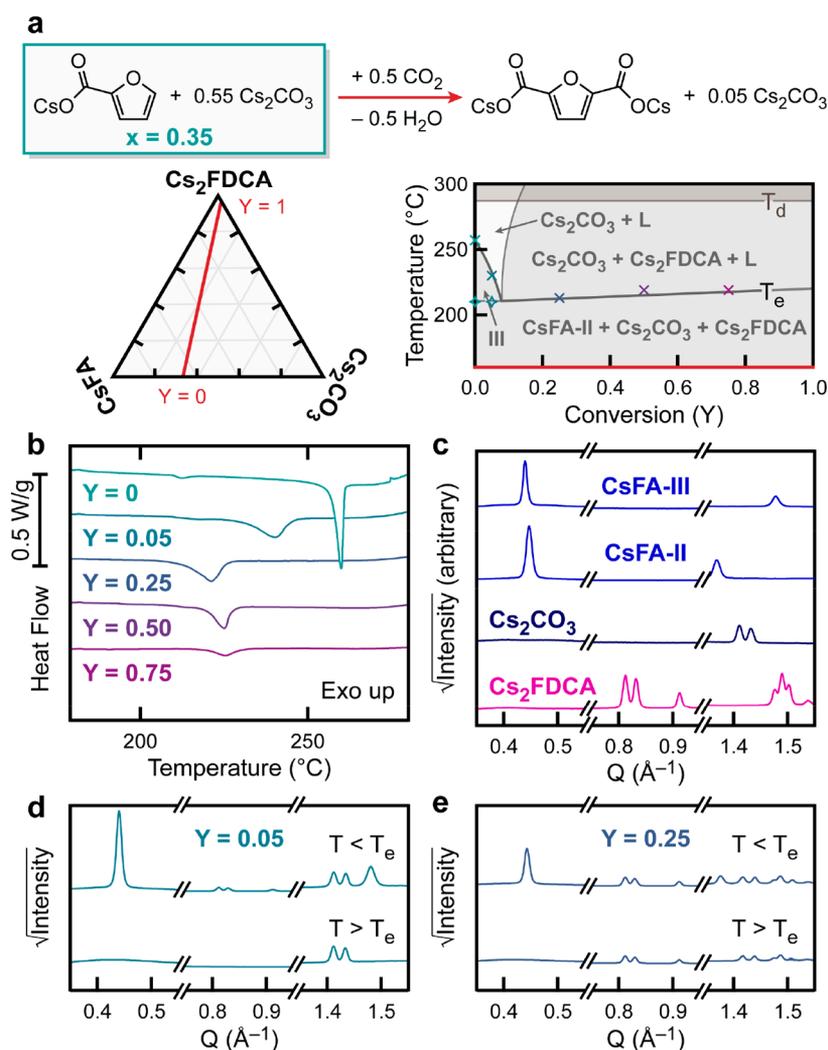


Figure 3. Phase equilibrium as a function of conversion in a ternary CsFA/Cs₂CO₃/Cs₂FDCA mixture. (a) Schematic representation of the cesium furoate carboxylation reaction as a cross section of ternary phase space. Regions in the phase equilibrium diagram (bottom right) are labeled with their constituent phases, where “L” corresponds to the molten eutectic phase. Region “III” corresponds to the three-phase region consisting of solid CsFA-III, Cs₂CO₃, and Cs₂FDCA. (b) DSC thermograms comparing eutectic melting transitions in the ternary mixture as a function of conversion. (c) Elevated-temperature PXRD patterns of individual components of the ternary mixture. Selected regions of the patterns are shown that allow for identification of the constituent crystalline phases in patterns of multicomponent mixtures. Patterns shown for Cs₂CO₃ and Cs₂FDCA are for their anhydrous, high-temperature forms. (d and e) PXRD patterns comparing ternary mixtures with $Y = 0.05$ and $Y = 0.25$, respectively, before and after eutectic melting, demonstrating that Cs₂FDCA is fully dissolved in the melt only at low conversion.

only a small fraction of the Cs₂CO₃ base. It should be noted that although a two-phase region of coexistence between solid Cs₂CO₃ and molten eutectic is present, the liquidus temperature at which the mixture would theoretically become uniformly molten can never be reached because it lies well beyond the thermal decomposition temperature of CsFA.

In contrast to the CsFA/Cs₂CO₃ system, the analogous mixture with $M = K$ does not exhibit a stable eutectic melt. The absence of eutectic melting was demonstrated using variable-temperature PXRD. When a mixture of KFA and K₂CO₃ with $x = 0.35$ was heated, the peaks corresponding to the furoate component eventually disappeared, while the carbonate peaks remained. However, unlike in the cesium-containing mixture, in this case the peaks corresponding to the furoate component did not reappear upon immediate cooling, indicating KFA decomposition rather than a reversible eutectic melting event (Figure 2e). In other words, the addition of K₂CO₃ to KFA does not sufficiently depress the KFA melting

point to create a stable two-phase region containing molten KFA below its decomposition temperature.

At elevated temperatures and in the presence of CO₂ gas, a mixture of CsFA and Cs₂CO₃ will begin to convert to Cs₂FDCA. If the reaction is performed under flowing conditions, the water produced as a byproduct of carboxylation is stripped away, and the carboxylation process can be envisioned as an interaction between gaseous CO₂ and a three-component mixture of anhydrous salts: CsFA, Cs₂CO₃, and Cs₂FDCA. In an ideal scenario in which the reaction proceeds with 100% selectivity to form exclusively Cs₂FDCA, the progression of the reaction from starting material to full conversion can be represented as a traversal through ternary phase space^{24,25} with a compositional constraint dictated by the 2:1 stoichiometric relationship between CsFA and Cs₂CO₃ (Figure 3a). We examined the phase equilibrium of this ternary system by performing thermal and PXRD analysis on samples of CsFA/Cs₂CO₃/Cs₂FDCA mixtures with compositions

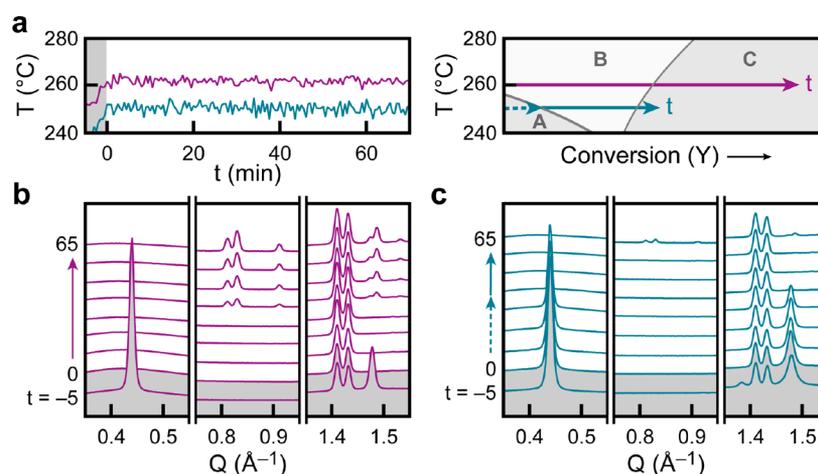


Figure 4. Operando PXRD analysis of cesium furoate carboxylation. (a) Measured temperature profiles of two *operando* PXRD experiments (left) and representation of ternary phase regions traversed at each temperature (right). Both experiments were performed by heating mixtures of CsFA and Cs_2CO_3 ($x = 0.35$) while flowing CO_2 gas through the sample capillary at 5 sccm and collecting diffraction images at 30 s intervals. For each experiment, time zero is defined as the point at which the set point temperature was first reached. Phase regions in the diagram correspond to (A) CsFA-III, Cs_2CO_3 , and Cs_2FDCA , (B) Cs_2CO_3 and eutectic melt, and (C) Cs_2CO_3 , Cs_2FDCA , and eutectic melt. (b and c) Selected PXRD patterns showing the evolution of crystalline phases for reactions carried out with set point temperatures of 260 and 250 °C, respectively.

designed to mimic the progression of a reaction starting from a binary CsFA/ Cs_2CO_3 mixture with $x = 0.35$.

Although Cs_2FDCA by itself is a crystalline solid in the temperature range relevant for CsFA carboxylation (Figures S14 and S15), conversion of the starting materials to Cs_2FDCA substantially alters the thermal transitions of the mixture compared to the CsFA/ Cs_2CO_3 binary phase system. DSC thermograms of anhydrous ternary mixtures prepared to mimic varying extents of conversion in the carboxylation reaction (defined here as Y , $0 \leq Y \leq 1$) show that the accumulation of even small amounts of Cs_2FDCA leads to depression of the system's eutectic temperature T_e below its value in the binary system (Figure 3b). With 25% of the starting CsFA converted to Cs_2FDCA , the mixture's eutectic temperature was decreased to 213 °C, which is ~ 43 °C below the CsFA/ Cs_2CO_3 binary eutectic melting point and within a few degrees of the transition between forms II and III of pure CsFA. Comparison of PXRD patterns taken before and after the eutectic transition in ternary mixtures with Y values of 0.05 and 0.25 illustrates which crystalline phases are present in the mixture before and after eutectic melting (Figure 3c–e). This comparison affirms that eutectic melting of the CsFA component at higher values of Y occurs directly from CsFA-II, bypassing the CsFA-III polymorph. An additional observation that emerges from this PXRD analysis is that a distinct region exists at low conversions for which the Cs_2FDCA salt is fully soluble in the eutectic melt. Eutectic melting in a mixture with $Y = 0.05$ presents as the disappearance of diffraction peaks that can be attributed to both CsFA-III and Cs_2FDCA components (Figure 3d). For a mixture with $Y = 0.25$, however, Cs_2FDCA diffraction peaks remain even after the disappearance of crystalline CsFA-II (Figure 3e). While increasing conversion leads to a decrease in the eutectic melting temperature, the molten eutectic fraction decreases as the mixture becomes increasingly rich in Cs_2FDCA . This effect can be seen from the decreasing peak area of the endothermic event associated with eutectic melting (Figure 3b). In other words, the carboxylation of CsFA occurs in a mixture that changes its phase composition as a function of conversion. The unique reaction medium is initially a heterogeneous blend of solid and molten

material that becomes progressively less molten in character as full conversion is approached.

Finally, we looked to directly observe the carboxylation of CsFA using *operando* PXRD. The results of these studies are consistent with the ternary phase equilibrium model based on the analysis presented above of ternary mixtures that mimic different extents of conversion, and additionally demonstrate some interesting properties of CsFA as a solvent-free reactant. In two separate experiments, mixtures of CsFA and Cs_2CO_3 with $x = 0.35$ were heated while flowing CO_2 through the sample capillary at 5 sccm. Following an initial ramp up to the chosen reaction temperature, each sample was held at its set point for 70 min while diffraction images were collected continuously. The two chosen set points were 260 and 250 °C, above and below the eutectic temperature of the CsFA/ Cs_2CO_3 binary mixture, respectively (Figure 4a). As expected, when the reaction was conducted at 260 °C, eutectic melting occurred during the temperature ramp, just prior to reaching 260 °C. As the reaction proceeded and conversion increased, no significant changes were initially observed in the sample's PXRD pattern. However, peaks corresponding to crystalline Cs_2FDCA became visible after approximately 30 min at the reaction temperature had elapsed (Figure 4b). Thus, starting from the binary eutectic melt, carboxylation forms FDCA^{2-} that is initially dissolved in the melt. As conversion increases, a saturation point is reached (somewhere between $Y = 0.05$ and $Y = 0.25$) and crystalline Cs_2FDCA forms as an additional phase.

When a fresh sample was heated instead to 250 °C under flowing CO_2 , no melting event was initially observed. We anticipated that no Cs_2FDCA formation would occur in the absence of this initial eutectic melting. Surprisingly, after approximately 35 min at 250 °C, spontaneous melting of the CsFA component was observed. As no appreciable change to the sample's temperature occurred during this interval, the occurrence of this melting event must have been induced instead by a change in the mixture composition. At the conclusion of the 70 min reaction period, peaks corresponding to crystalline Cs_2FDCA became barely visible in the PXRD pattern, confirming that carboxylation occurred over the course

of the experiment (Figure 4c). This result highlights the melting temperature depression induced by even small amounts of Cs_2FDCA . In addition, it suggests that a small degree of reactivity is possible between CsFA-III and Cs_2CO_3 even without the formation of bulk eutectic domains between the two salts. Relative to lower-temperature polymorphs of CsFA and the solid forms of KFA, CsFA-III shows only weak crystalline ordering (Figures S9 and S10), which may be sufficient to enable CsFA to participate in intermolecular reactions.

Integrating the results presented above, Figure 5 depicts the evolution of the phase composition for an idealized CsFA

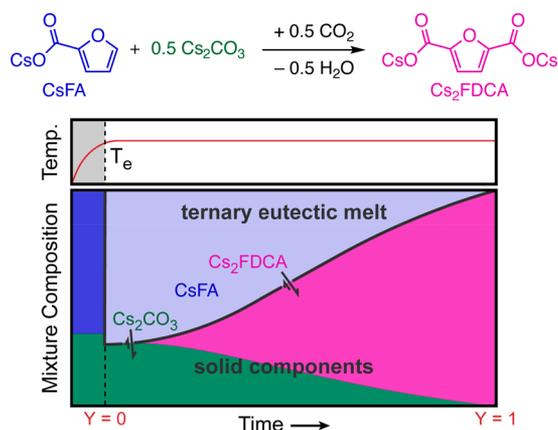


Figure 5. Evolution of the reaction mixture during solvent-free carboxylation of cesium furoate.

carboxylation reaction performed at a temperature just beyond the binary eutectic melting temperature. Upon reaching the eutectic melting temperature, the initial mixture of solid CsFA and Cs_2CO_3 undergoes a transition into a mixture of solid and molten components. The molten phase is initially a binary eutectic composed primarily of the low-melting CsFA with a minor amount of Cs_2CO_3 ; most of the Cs_2CO_3 remains in its solid, crystalline form. As the reaction begins and Cs_2FDCA is formed, it is initially dissolved in the molten phase. With increased conversion, Cs_2FDCA saturates the molten phase and precipitates to form crystalline Cs_2FDCA as an additional solid phase. The reaction proceeds in the ternary eutectic phase with the minor eutectic components (Cs_2CO_3 and Cs_2FDCA) in equilibrium with their corresponding solid phases. Increasing conversion leads to the gradual consumption of the ternary eutectic and solid Cs_2CO_3 components of the mixture as the amount of solid Cs_2FDCA increases.

The idealized reaction presented in Figure 5 does not account for the small to moderate amounts of decomposition products that are typically observed along with the target Cs_2FDCA product, which complicate the reaction mixture composition.^{10,11} Some of these decomposition products are small-molecule carboxylate salts (e.g., formate, acetate, and malonate) that are comparatively low-melting and might alter the phase behavior of the molten component of the reaction mixture. However, the most significant byproduct observed is dense, polymeric char that adds an additional solid component to the heterogeneous mixture. Notwithstanding these additional complexities, the components investigated in the experiments described above make up the majority of the material present in the CsFA carboxylation reaction.

The observation of CsFA carboxylation for a reaction performed below the binary eutectic melting temperature (Figure 4c) suggests that it is possible for intermolecular reactions to occur between two solid phases (in this case CsFA-III and Cs_2CO_3). Carboxylation of CsFA initially proceeds in this ostensibly all-solid mixture until formation of a very small amount of the product Cs_2FDCA induces melting as a ternary eutectic. Evidence for intermolecular reactions between species in two solid phases has been reported previously,^{26–29} although in these cases mechanical energy (e.g., ball milling) was needed to observe reactivity.

The higher melting point of KFA makes it infeasible to perform carboxylation with only KFA and K_2CO_3 because a eutectic cannot be accessed before decomposition. However, we have shown previously that adding a stoichiometric quantity of potassium isobutyrate to the KFA and K_2CO_3 mixture enables carboxylation to occur.¹⁰ Additionally, carboxylation can be performed in high yield using salts composed of furoate and carbonate with a mixture of K^+ and Cs^+ cations, even when only a small proportion of Cs^+ salts is used.¹¹ While characterizing the phase behavior of these more complicated systems is beyond the scope of this study, the additional degrees of freedom created by using two cations or introducing another anion are expected to give rise to a relatively low-melting eutectic that enables the reaction to proceed.^{24,25} We note that the fraction of the salt mixture that exists in a molten state may be small enough such that there is no visible bulk melting event during a reaction. Regardless of composition, however, furoate carboxylation results in sintering of the salt particles, which is consistent with the formation of molten components during the reaction.

Finally, the results presented above illuminate the factors that must be addressed in scaling furoate carboxylation. When the carboxylation is performed under quiescent conditions, the evolution of the phase components over time creates mass transport limitations. Specifically, as the amounts of the ternary eutectic and solid Cs_2CO_3 phases decrease and the solid Cs_2FDCA product accumulates, mass transport of CO_2 and carbonate into the molten phase is expected to become increasingly difficult. Reactor design must therefore take into account the variation in mixture heterogeneity as a function of conversion and maintain a large effective contact area among the molten phase, the CO_2 gas, and the Cs_2CO_3 phase. Reactors that continuously mix or grind the reaction components may be especially useful in this regard.^{30,31}

The combination of PXRD and thermal analysis techniques has provided a detailed description of the phase composition of solvent-free furoate carboxylation. The results demonstrate that the reaction occurs in a molten phase dominated by CsFA with smaller amounts of the Cs_2CO_3 reactant and Cs_2FDCA product. The diminution of the molten component and solid Cs_2CO_3 component as the reaction forms solid Cs_2FDCA presents challenges for maintaining efficient mass transport that need to be managed to achieve optimal yields on a large scale. The strategy for analyzing furoate carboxylation described here can be applied to other solvent-free systems to help identify compositional and operational changes that improve performance.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcllett.0c02210>.

Experimental methods, crystallographic information for potassium furoate, structure solution and refinement details for cesium furoate, supplementary thermal analysis data, and variable-temperature PXRD contour plots (PDF)

Crystallographic information for potassium furoate (CIF)

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Notes

The authors declare the following competing financial interest(s): The authors have filed a provisional patent application based on findings in this work.

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