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REGULAR ARTICLE

Computational study on the mechanism of the reaction of carbon dioxide with siloxy silanes

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Abstract The reaction of carbon dioxide with α-siloxy silanes assisted by cesium fluoride is studied by means of DFT calculations with the B97D functional. Different mechanistic models are examined, including explicit introduction of cationic counterions and solvent molecules. The reaction is confirmed to proceed through carbanionic intermediates generated by Brook rearrangement, a carbon-to-oxygen transfer of a silyl group. The cesium cation is shown to play a critical role in stabilizing the key transition state.

Keywords CO_2 activation · DFT · Brook rearrangement · Counterions

1 Introduction

CO_2 is one of the most abundant and cheap carbon sources on earth. It is moreover nontoxic and easily renewable. Because of this, there has been a growing interest in utilizing the CO_2 as a C1 feedstock for the chemical industry [1–8]. The most sustainable and promising approach to an innovative use of CO_2 is the establishment of pathways for the chemical industry where nonrenewable fossil-based sources are currently used. Reactions have been developed for effective CO_2 incorporation into the synthesis of various organic compounds such as carboxylic acid derivatives and (poly) carbonates [9–14]. Among those applications, reactions that form C–C bonds by the functionalization of alkenes, alkynes, allenes, organohalides, organometallic reagents to generate carboxylic acids play a prominent role [15–22].

In recent years, carboxylation with organosilanes has attracted some attention. Several organosilanes have been used as nucleophiles for the synthesis of various carboxylic acid derivatives such as propiolic acid [23], benzyl carboxylic acid [24], α-amino acids derivatives [25], cyclopropane carboxylic acids [26] and α-hydroxy acid derivatives [27]. All these reactions have utilized CsF as the fluoride source for the activation of the C–Si bond. Among the several reactions reported for the synthesis of α-hydroxy acid derivatives, [28–30], we are particularly interested in the remarkable synthesis of α-hydroxy acids and esters recently proposed by Sato and co-workers. The reaction operates through fluoride-mediated CO_2 incorporation to α-siloxy silanes (Scheme 1) [27]. The use as reactants of the readily available and easy to handle organosilanes along with the abundant, inexpensive and renewable CO_2 is appealing factors. α-hydroxy acids are useful building blocks in organic synthesis [31, 32]. They are used in the synthesis of species such as glycolic acid and mandelic acid which are of great commercial significance [33]. Moreover, α-hydroxy acids are also used as precursors in the preparation of aldehydes via oxidative cleavage [34, 35] and have a wide range of applications in the cosmetic industry [36]. The proposed

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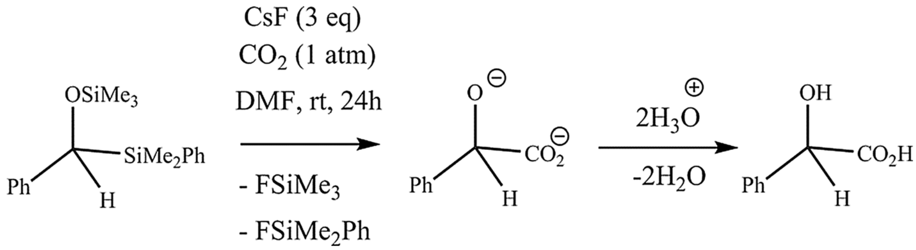
Scheme 1 Carboxylation reaction of α-siloxy silane reported by Sato and Co-workers



mechanism by Sato and co-workers for the process is shown in Scheme 2, where the role of a key carbanionic intermediate is highlighted. This intermediate is obtained from an anionic α-silyl alkoxy species by Brook rearrangement. The Brook rearrangement is the intramolecular anionic migration of a silyl group from carbon to oxygen in the presence of a base [37, 38]. The greater strength of the oxygen–silicon bond compared to the carbon–silicon bond provides the driving force for the conversion of silyl carbinols to the corresponding silyl ethers. The carbanionic intermediate is able to carry out a nucleophilic attack on CO_2 to form the dianion. The final product α-hydroxy acid is then obtained by the reaction of dianion with two protons from the acidic medium (HCl/H_2O which is added during the workup process).

Although the main mechanistic trends seem clear, there are a number of intriguing features in the reaction which may be important for the extension of its scope. It would be relevant to confirm the existence of the anionic intermediates and to identify the rate limiting step. The exact role of the cesium fluoride excess is moreover intriguing. Calculations have been previously used in our group in both fluoride [39] and carbon dioxide chemistry [40]. Herein, we report a complete DFT study on the reaction in order to investigate these points.

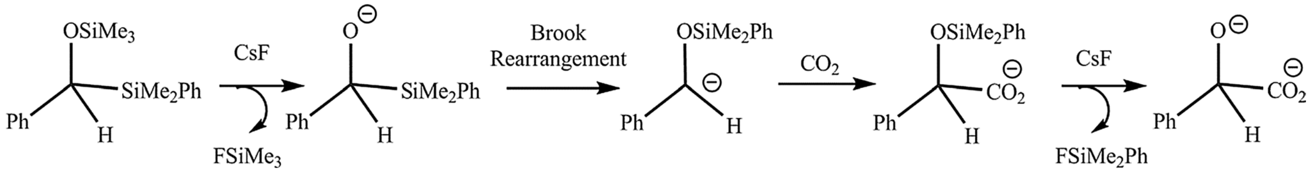
2 Computational details

All the calculations were carried out through density functional theory [41] with the B97D [42, 43] functional employing the Gaussian 09 suite of programs [44]. Geometry optimization of all the stationary points was carried out with an implicit solvent phase (DMF, $\varepsilon = 37.219$) introduced with SMD [45]. The LANL2DZ [46–48] basis set with the effective core potential was applied for Cs, and 6–31 + g(d) [49–53] basis set was used for all other atoms. The use of a basis set with double-ζ description complemented with diffuse functions is appropriate for an electronically simple reaction like this one. The B97D, including dispersion, is also state of the art for this type of chemistry. Transition states were characterized by a unique imaginary frequency, which was verified to represent the desired reaction coordinate in each case. All the minimum energy structures such as the intermediates, reactants and products were confirmed to exhibit no imaginary frequency. The connectivity between minima and transition states was confirmed by geometry optimizations after small displacement in the direction of the reaction coordinate from the transition state. Gibbs free energy corrections were computed at standard conditions of temperature ($T = 298$ K) and pressure ($p = 1$ atm). A dataset collection of computational results is available in the ioChem-BD repository [54] and can be accessed via doi:10.19061/iochem-bd-1-36.

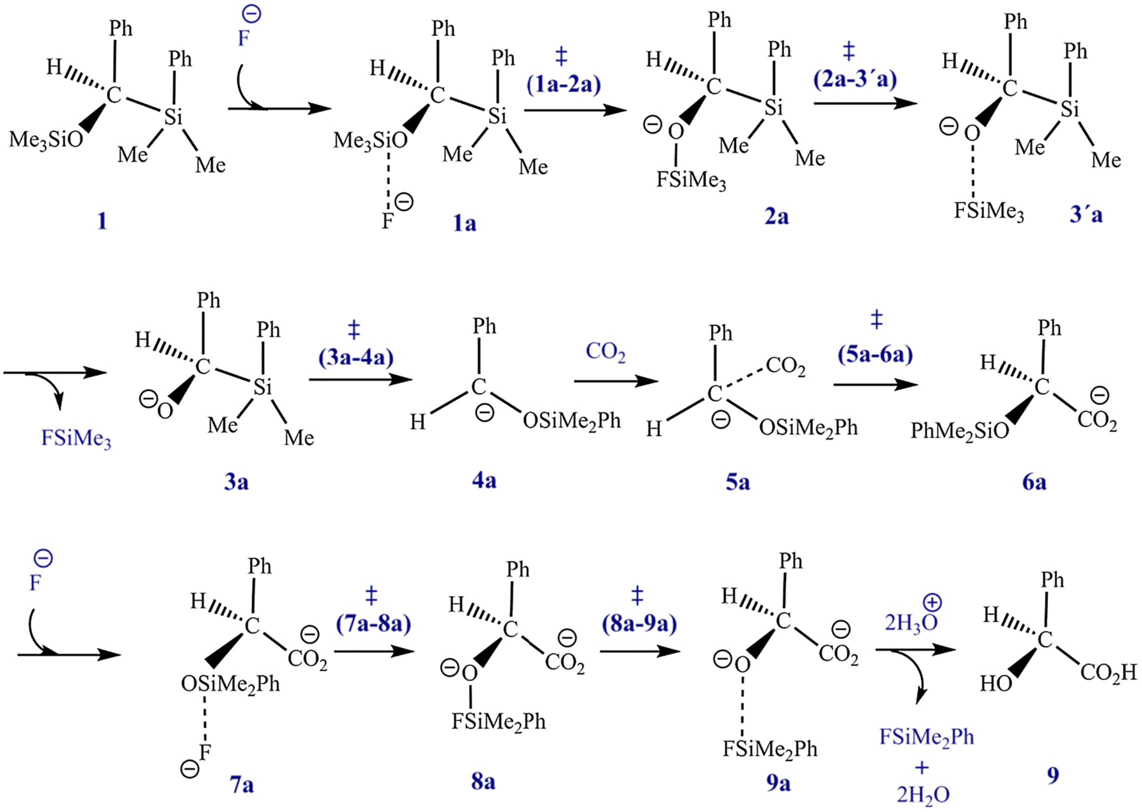
3 Results and discussion

A first set of calculations was carried out on the experimentally proposed mechanism, without explicit involvement of the Cs^+ counterions and solvent. The results are summarized in Scheme 3 and Fig. 1. The reaction follows indeed the proposed mechanism, as shown in Scheme 3. First, CsF releases a fluoride anion attack into the α-siloxy silane reactant (1) resulting in the formation of adduct 1a.

The silyl group is then coordinated to F through transition state (1a–2a), which leads to the species 2a, which is characterized by the presence of a F–Si bond. It is worth noticing here that, according to our calculations, $O–SiMe_3$



Scheme 2 Experimentally suggested mechanism



Scheme 3 Reaction scheme for the reaction without involvement of the counterion

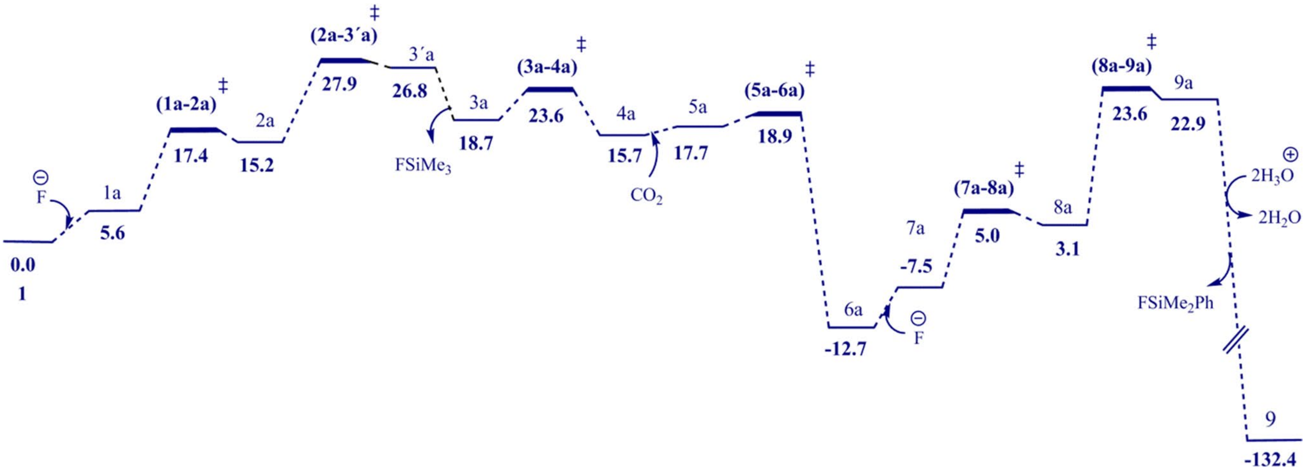


Fig. 1 Free energy profile for the reaction without involvement of the counterion

group is more easily activated by fluoride rather than the C–SiMe$_2$Ph group. This is hardly surprising as the O–Si bond is expected to be more polar than the C–Si bond. The silyl group is then completely transferred from O to F through transition state (2a–3′a). The species 3′a is an adduct between an alkoxy anion and the FSiMe$_3$ molecule. Release of the weakly bound FSiMe$_3$ molecule in 3′a leads then to the α-silyl alkoxy anion 3a, which is ready to undergo the Brook rearrangement. In the Brook rearrangement, the silyl group is transferred from carbon to oxygen, leading to carbanion 4a.

This carbanion is then able to undertake a nucleophilic attack on the central atom of a carbon dioxide molecule through transition state 5a–6a. The carboxylate anion 6a still contains a silyl unit, which is again eliminated from the system with the help of an external fluoride anion. The attack of the second fluoride ion results in the formation of adduct 7a. The silyl group is then coordinated to F via transition state (7a–8a) to form dianion 8a. 8a rearranges through a O-to-F silyl transfer in transition state (8a–9a). The resulting dianion 9a reacts with two protons from the acidic medium (HCl/H_2O which is added during the workup process is the proton source, and we have represented it as H_3O^+ in the calculation) to result into the desired product α-hydroxy acid 9.

The qualitative features in Fig. 1 respond to expectations, but the quantitative ones do not. The computed kinetic barrier for the whole process is 36.3 kcal/mol, the difference between the free energies of reactant 6a and transition state 8a–9a, corresponding to the second desilylation step. This is too high for a reaction happening at room temperature. The barrier from the reactant 1 to transition state 2a–3′a corresponding to the first desilylation step is 27.9 kcal/mol, which is also in the limits of what could be deemed acceptable for a reaction at room temperature. It is unlikely that the applied functional is so inaccurate for this type of system. In order to improve the agreement between calculation and experiment, we decided to reexamine the computational model.

Fluoride plays certainly a critical role in the process, and its strong bond to silicon is a thermodynamic driving force for the whole process and plays a key kinetic role favoring the individual silyl transfer steps. But fluoride is obviously not introduced as a free anion, but as part of a salt, cesium fluoride in the experimental case we are studying. We considered thus the role that the introduction of an explicit cesium cation in the computational model may have in the overall process [55]. The introduction of a naked cesium cation would still be misleading, as it is likely coordinated by DMF solvent molecules [56]. We explored computationally the cesium coordination number by trying with up to six DMF molecules and found that the preferred number of solvent molecules around cesium is four for the naked cation and two when interacting with the rest of the system (for more details on the number of solvent molecules, see Supporting Information). The interaction between $Cs(DMF)_2^+$ and intermediate 1a, resulting in adduct 1b, is highlighted in Fig. 2. The Cs^+ center has favorable cation-π interactions with the two phenyl groups in α-siloxy silane.

The mechanism computed when introducing the cesium species is summarized in Scheme 4 and Fig. 3. The basic mechanistic steps are the same discussed above (in Scheme 3) for the reaction without cesium. But there are significant quantitative differences in the free energy profile.

We focus on the differences concerning the two highest barriers. The barrier associated transition state (2b–3′b) corresponding to the first desilylation is 21.7 kcal/mol (measured from 1b), clearly below the 27.9 kcal/mol associated with transition state (2a–3′a). This lowering can be tracked down first to the stability of adduct 1b, which is 12.5 kcal/mol more stable than the separate reactants. This is in sharp contrast with 1a, without Cs^+, which was 5.6 kcal/mol above reactants. This 5.6 kcal/mol is no longer necessary when cesium is introduced in the system, which leads to a lower barrier for this step. Even more critical is the improvement in the barrier associated with transition state (8b–9b), corresponding to the second desilylation. In this case, the barrier with cesium is 18.1 kcal/mol (measure from 7b). This is a very substantial improvement from the 36.3 kcal/mol difference between 6a and (8a–9a). In this case, some stabilization can be also attributed to a superior stabilization of the intermediates involving fluoride incorporation into the system. In particular, 7a was 5.2 kcal/mol

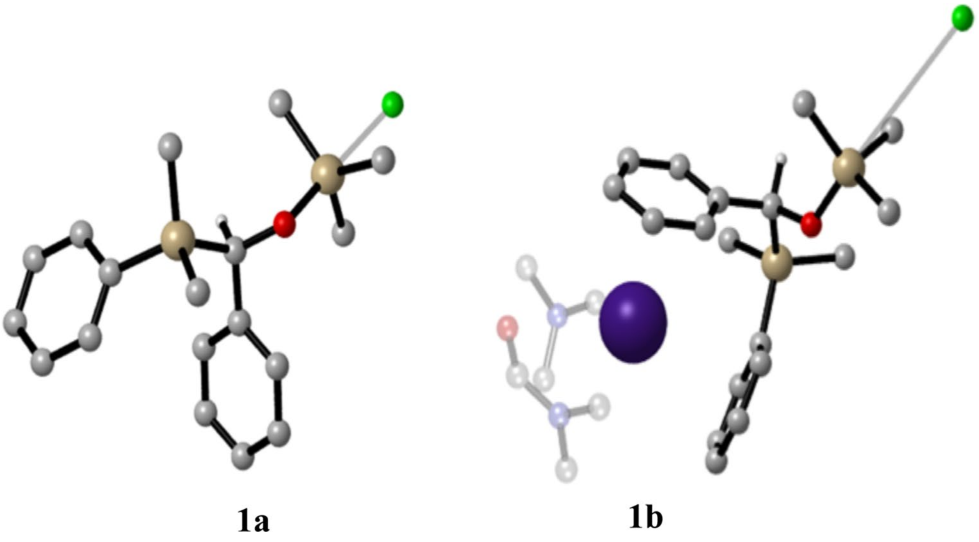
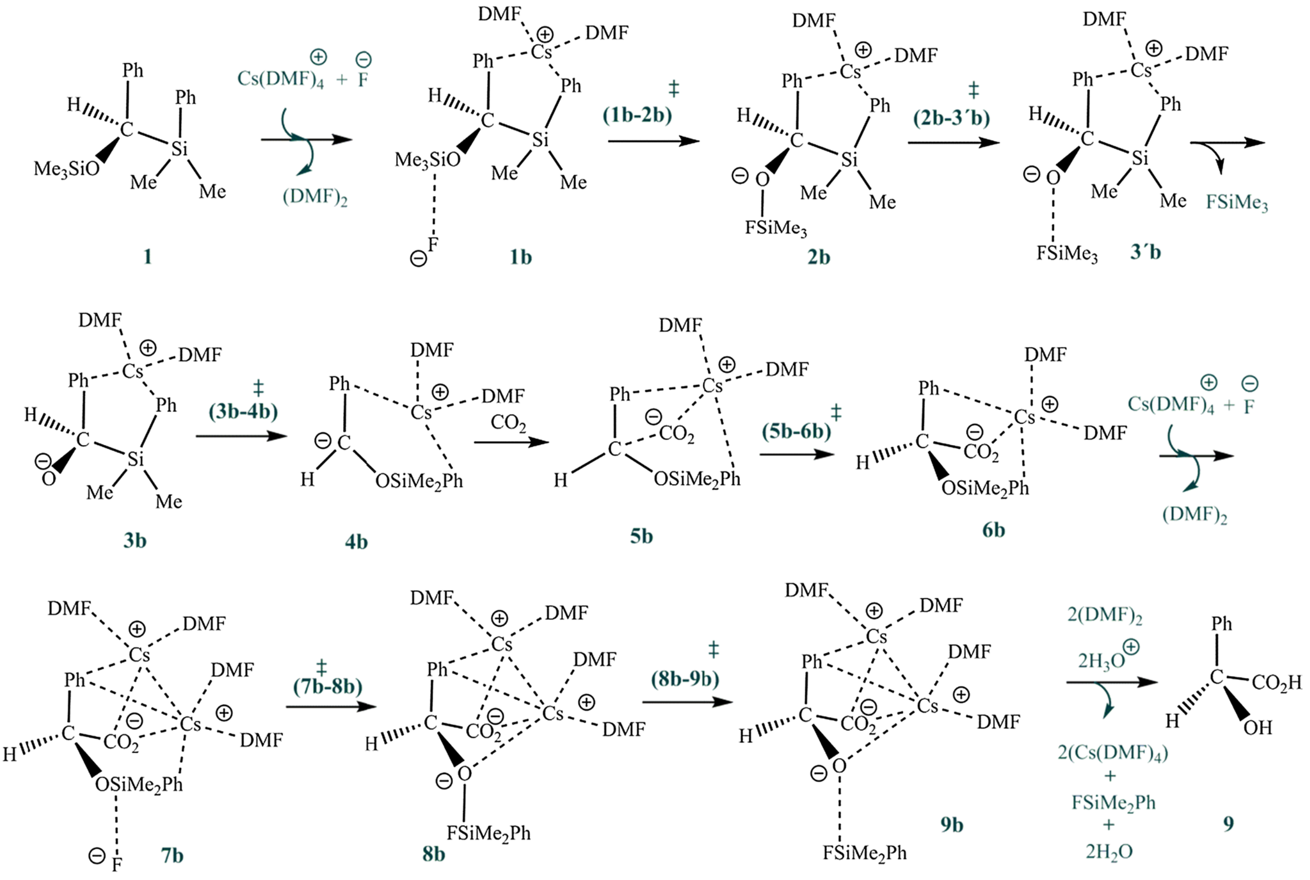


Fig. 2 Optimized structures of the intermediates **1a** and **1b**



Scheme 4 Reaction scheme for the reaction with involvement of the Cs^+ counterion

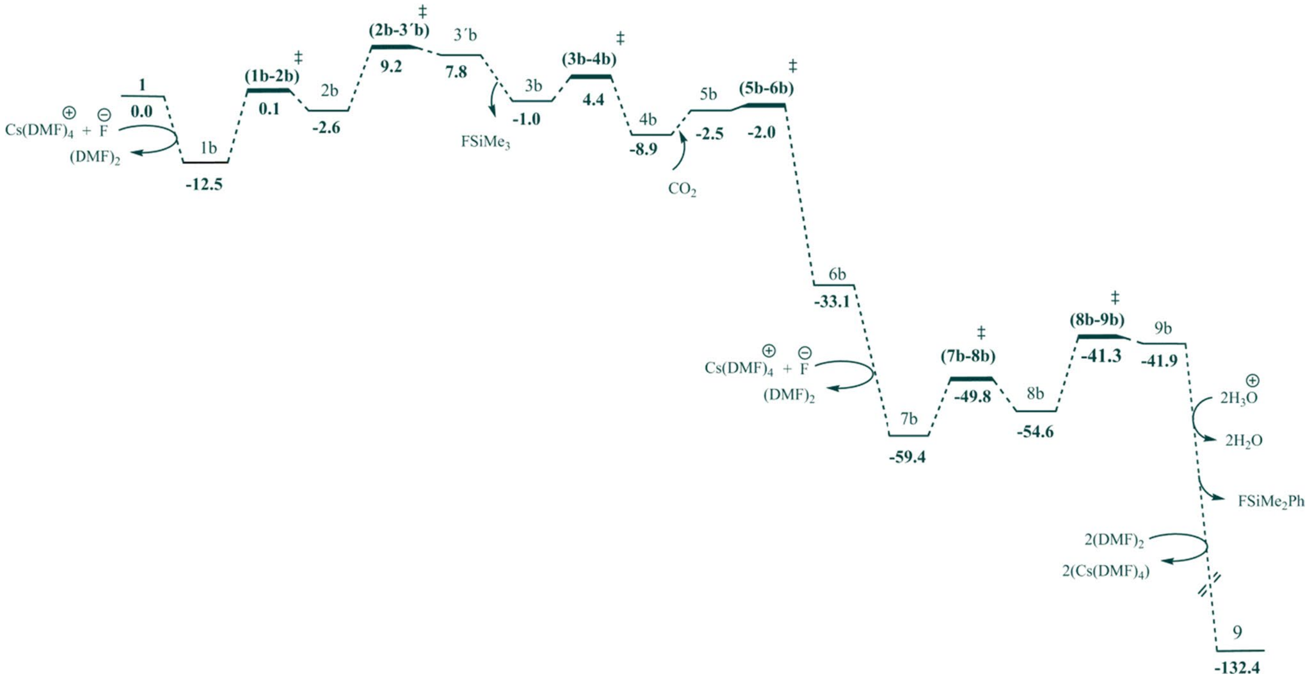


Fig. 3 Free energy profile for the reaction with involvement of the Cs^+ counterion

above 6a, while 7b is 26.3 kcal/mol below 6b. But the key difference seems related to a specific stabilization of the transition state (8b–9b) with respect to the preceding intermediate 8b. The release of the $FSiMe_2Ph$ leaves a more anionic character on the oxygen center, which in turn strengthens its interaction with the positive charge at cesium.

The remaining highest barrier in the catalytic cycle is then 21.7 kcal/mol, which is fully compatible with the experimental observation of a reaction taking place at room temperature. The presence of Cs^+ is thus critical for the reaction to take place. It stabilizes sufficiently the key transition state for the reaction to be complete. The importance of the presence of the seemingly innocent counterions in reaction mechanisms is in this way confirmed [57, 58].

4 Conclusions

The mechanism of the fluoride-assisted carboxylation reaction between α-siloxy silanes and carbon dioxide to form α-hydroxy acids has been computationally characterized. Calculations confirm the fundamental role of a Brook rearrangement step, where a silyl group is transferred from carbon to oxygen, resulting in a carbanionic intermediate. This carbanionic center is the responsible of a low barrier nucleophilic attack on the central atom of carbon dioxide. Calculations have also revealed the unexpected importance of the cesium cation in the reaction. In particular, the seemingly innocent counterion in the fluoride salt plays a critical role. The cesium cation that was used in experiment has to be explicitly considered in the calculation in order to reproduce the experimental result.

The highest energy barriers of the overall process correspond to the two desilylation steps, where the silyl substituents are abstracted by fluoride anions from the organic system. Once the first silyl group is abstracted, the Brook rearrangement takes place with very low barrier. After that, the reaction can be completed by abstraction of the second silyl group. The key role of these abstraction steps is consistent with the requirement of a halide with affinity for silicon such as fluoride for the reaction to take place. The importance of the anion in the reactivity explains moreover the relevance of the nature of the associated countercation.

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