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Carbon Kinetic Isotope Effects and the Mechanisms of Acid Catalyzed Decarboxylation of 2,4-Dimethoxybenzoic acid and CO Incorporation into 1,3-Dimethoxybenzene

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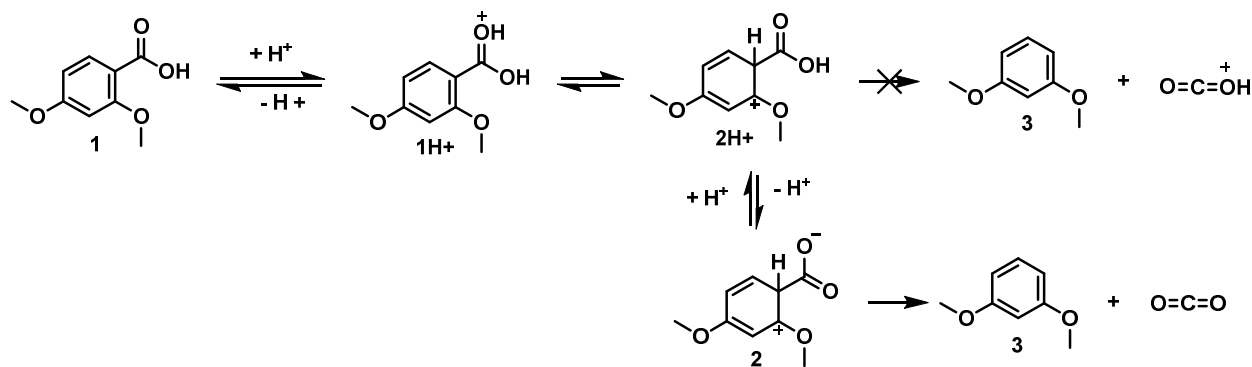
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26 **Abstract:** The rate of decarboxylation of 2,4-dimethoxybenzoic acid (**1**) is accelerated in parallel
27 to the extent that the carboxyl group acquires a second proton (**1H**⁺). However, the conjugate acid
28 would resist C-C bond breaking as that would lead to formation of doubly protonated CO₂. An
29 alternative via formation of a higher energy protonated phenyl tautomer (**2H**⁺) prior to C-C bond
30 breaking would produce protonated CO₂, an energetically inaccessible species that can be avoided
31 by transfer of the carboxyl proton to water in the same step. Headspace sampling of CO₂ that
32 evolves in the acid catalyzed process and analysis by GC-IRMS gives smaller than expected value
33 of 1.022 for the carbon kinetic isotope (CKIE), k^{12}/k^{13} . While this value establishes that C-C
34 cleavage is part of the rate-determining process, intrinsic CKIEs for decarboxylation reactions are
35 typically greater than 1.03. Computational analysis of the C-C bond cleavage from **2H**⁺ gives an
36 intrinsic CKIE of 1.051 and suggests two partially rate-determining steps in the decarboxylation
37 of **1**: transfer of the second carboxyl proton to the adjacent phenyl carbon and C-C cleavage in
38 which the carboxyl proton is also transferred to water. Applying the principle of microscopic
39 reversibility to fixation of CO₂ in acidic solutions reveals the importance of proton transfers to
40 both carbon and oxygen in the overall fixation process.
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■ INTRODUCTION

Decarboxylation reactions in water typically occur as electrophilic substitution processes in which rate-determining loss of CO₂ from a carboxylate is followed by protonation or oxidation of the residual anion.¹ In those cases, catalysts can promote decarboxylation by better accommodating the electrons that are gained from the bond that is broken upon release of CO₂.²⁻⁷ An alternative pattern occurs in the decarboxylation of activated benzoic acids. In solutions of moderate acidity, rates of decarboxylation depend on the concentration of the un-ionized carboxyl group.^{8,9} We expect that the proton on the un-ionized carboxyl group will prevent direct formation of CO₂, requiring an alternative mechanism. Those reactions are likely to proceed via a transition state that occurs after tautomerization of the aromatic carboxylic acid. The process involves loss of aromaticity by protonation of the phenyl group adjacent to the carboxyl, leading to direct loss of CO₂ from the minor tautomer. If the reaction were to proceed to a transition state directly from the neutral carboxyl group, a product would be the inaccessible conjugate acid of CO₂, HOCO⁺ (“protonated CO₂”), a species that is much too acidic to exist in solution (pK_A<-30).^{10,11} A detailed knowledge of the mechanism of this catalytic route applies to the potentially important reaction in which acids catalyze the fixation of CO₂ onto benzene derivatives.

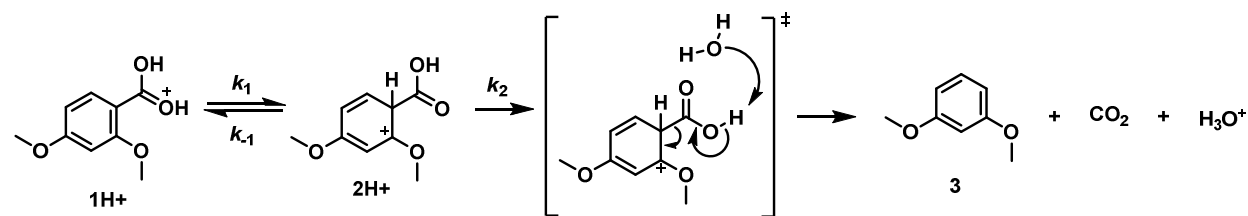
The decarboxylation of 2,4-dimethoxybenzoic acid (**1** in Scheme 1) in highly acidic solutions conforms to the rate law for a specific-acid catalyzed process.^{8,12} The rate increases with acidity in parallel with the expected extent of formation of the conjugate acid of **1** (**1H**⁺ in Scheme 1).^{9,12,13} For comparison, decarboxylation of **1** under neutral conditions also avoids release of protonated CO₂ but that results from a reactive tautomeric form (**2** in Scheme 1).⁸ It is not obvious how increasing acidity would accelerate the reaction based on this neutral mechanism. Yet, the observed increase in rate with acidity indicates that increasing the extent to which **1** is converted to its carboxyl-protonated conjugate acid¹⁴ is associated with lowering the energy of the rate determining transition state. The observation also implies that the proton of the carboxyl group is present in the transition state that produces C-C bond cleavage (Scheme 2). Still, the transition state must not produce protonated CO₂.¹¹

Scheme 1 – Rate-determining proton transfer converts the unreactive form of DMBA (**1**) to the reactive tautomer (**2**) in which the C-C bond cleaves to form 1,3-dimethoxybenzene (**3**) and CO₂.



We previously proposed potential mechanisms for acid catalyzed decarboxylation of **1** that avoid formation of protonated CO₂.⁸ Based on the results of computations, we concluded that the most favorable transition state involves the combined cleavage of the C-C bond of **2H⁺** and transfer of the carboxyl proton to water (Scheme 2).⁸

Scheme 2 – The C-C bond cleavage occurs from the ring-protonated tautomer of **1H⁺** with simultaneous deprotonation of the carboxyl group by solvent water. This mechanism is consistent with the observed acid catalysis and avoids the formation of protonated CO₂.



Determinations of k^{12}/k^{13} carbon kinetic isotope effects (CKIEs) for the formation of CO₂ in decarboxylation reactions also help to reveal the nature of the transition states of the acid-promoted mechanism.^{15,16} Together with the transition state proposed from computations, we can use the magnitude of the CKIE to determine if the C-C bond cleavage step is competitive with other processes. We expect that transfer of the carboxyl proton to water can occur in the same transition state as C-C cleavage. As a result, the energy of the transition state would be likely to be comparable to those of a preceding proton transfer step.

We report CKIEs for the decarboxylation of **1** under conditions where (1) the neutral form (**1**) converts to the very reactive zwitterion tautomer and (2) the reaction proceeds from the conjugate

acid ($\mathbf{1H}^+$). We utilize head-space coupled isotope ratio mass spectral analysis of the evolved CO_2 . We follow the isotopic composition of the CO_2 produced over the course of the decarboxylation reaction.^{17,18} The acquired data provide information that is transformed to rate constants with application of the Rayleigh equations.¹⁷ The results provide accurate values needed to deduce the CKIEs of the reactions of interest.¹⁹

■ RESULTS AND DISCUSSION

The CKIE for the decarboxylation of **1** at high acidity, where the reactant is present in the form of its conjugate acid ($\mathbf{1H}^+$), is 1.022 (Table 1). In an important contrast, reactions that produce CO_2 directly from a carboxylate have values for intrinsic CKIEs that are > 1.03 .^{16,20} The smaller value for the acid catalyzed process most likely indicates that another step is partially rate-determining. In highly acidic solutions, steps in which proton transfers precede C-C bond breaking would not be kinetically significant if the reactant interconverts rapidly with the higher energy tautomer from which C-C bond cleavage occurs. Scheme 2 presents the case where the barrier associated with k_{-1} would be comparable to that for k_2 , reducing the observed CKIE from its intrinsic value. Alternatively, the C-C bond-cleaving step (k_2) occurs in concert with transfer of the carboxyl proton to water in a way that reduces the intrinsic CKIE. In the latter model, the lower CKIE is consistent with a smaller difference in C-C bonding in the transition state compared to the reactant state than in reactions without proton transfer. Since the isotope effect could reflect differences in bonding,²⁰ the measured value would be consistent with considerable C-C bond character being present at the highest energy point on the lowest energy pathway.

Table 1. Carbon kinetic isotope effects (CKIEs) for the acid-catalyzed decarboxylation of 2,4-dimethoxybenzoic acid. The H_o values report the acidity of solutions based on the extent of protonation of aniline-derived indicators according to Hammett's acidity function.

H_o (HClO_4)	CKIE (± 0.002)
-2.62	1.022
-0.36	1.002

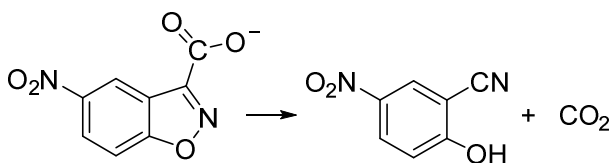
Marlier and O'Leary applied transition state analysis from CKIEs for decarboxylation reactions in general.²⁰ "The range of CKIEs is 1.03-1.07, where the carbon-carbon bond-making or -breaking process is entirely rate limiting: ...Carbon isotope effects in decarboxylation reactions increase

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3 as the transition state becomes more product-like. ...” The value we observe for the protonated
4 reactant is below the range of intrinsic values cited by Marlier and O’Leary, indicating that the C-
5 C bond cleavage is only partially rate-determining. We also observed a significant solvent isotope
6 effect for the reaction of 1H^+ at high acidity.⁸ It is therefore likely that the reduced CKIE is the
7 result of kinetically significant proton transfer.
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13 Our computational modelling of the decarboxylation of 2H^+ provides an intrinsic CKIE of 1.051
14 for the C-C bond breaking step that is accompanied by loss of proton. This is significantly larger
15 than the experimental value (1.022). The larger value is within the range that had been reported
16 for decarboxylation CKIEs in general.²⁰ Therefore, we conclude that the smaller CKIE results from
17 partially rate-limiting proton transfer in a step that forms the pre-decarboxylation intermediate.
18 This is consistent with the similar Gibbs free energies computed for the ring protonation and C-C
19 bond cleavage transition states.⁸
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27 Another basis for comparison of intrinsic CKIE values for C-C bond-cleavage is the
28 decarboxylation of Kemp’s 5-nitro-3-carboxybenzisoxazole²¹ (Scheme 3). This is a single-step,
29 irreversible process where C-C cleavage is achieved with no involvement of a catalyst in the
30 transition state. Under a very wide range of conditions, rate constants for the decarboxylation vary
31 over a ten thousand-fold range.¹⁶ In contrast, the CKIEs vary only to a very small extent, from
32 1.043 to 1.046.¹⁶ This provides a good estimate for the intrinsic CKIE of a process in which C-C
33 cleavage is considerable in the transition state and is also clearly rate determining.
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40 Scheme 3. The decarboxylation of 5-nitro-3-carboxybenzisoxazole is irreversible and
41 spontaneous, with protonation remote from the site of C-C cleavage.²¹
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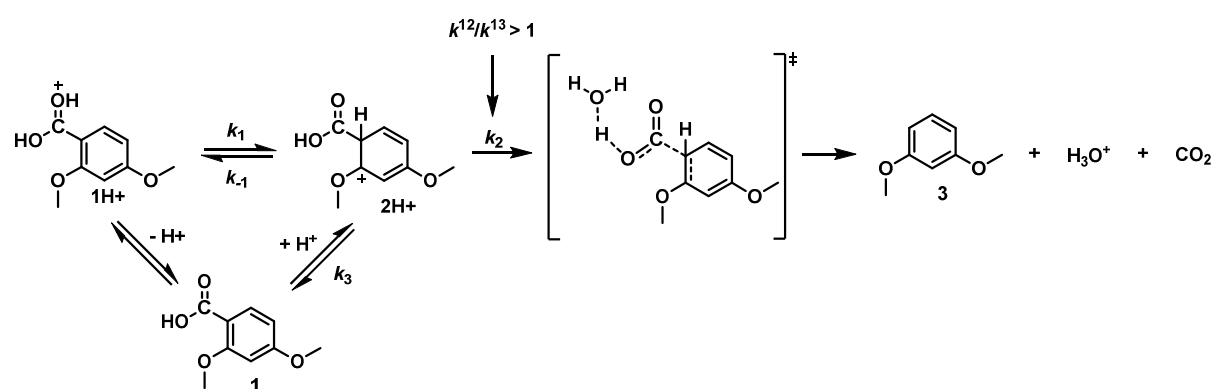


As the acidity of the solution is decreased, the CKIE becomes insignificant (Table 1), while the
SKIE becomes more substantial.⁸ This indicates that the decarboxylation of **1** in slightly acidic
solutions involves rate-determining proton transfers prior to or in the same step that releases CO_2 .

Collectively, these kinetic isotope effects are consistent with our previous proposal⁸ and support this unusual mechanism for catalysis of decarboxylation.⁸

Applying this information to deduce the detailed mechanism (Scheme 4), we propose that the C-C bond cleavage step includes transfer of the C-H on the carboxyl attached to the protonated phenyl group to water (k_3) or directly to the carboxyl (k_1). In either case, it is likely that the C-protonated phenyl group is highly energetic. Thus, transfer of the proton in the exergonic direction will have a rate constant that is near the diffusion limit.²² The significant solvent isotope effect confirms that proton transfer is kinetically significant. The observed rate constant at 60 °C is $2 \times 10^{-4} \text{ s}^{-1}$ under conditions where the carboxyl group of **1** is in the form of its conjugate acid. We estimate the pK_A of $\mathbf{1H}^+$ to be -3.5, based on the known values of related benzoic acids and the intramolecular hydrogen-bond based stabilizing effect of the methoxy group.⁸ The estimated pK_A of the ring-protonated tautomer is -9.⁸ Therefore, only one part in 10^6 of the protonated carboxyl species will be present as the C-protonated tautomer ($\mathbf{2H}^+$). Based on the observed rate constant and the fraction of species in the reactive form, $k = 2 \times 10^2 \text{ s}^{-1}$ for the decarboxylation step that proceeds directly from the reactive tautomer, the value of k_2 is less than the value for a thermodynamically favorable proton transfer.

Scheme 4. The pre-decarboxylation intermediate undergoes loss of a proton at a rate that is competitive with C-C bond cleavage of the carboxyl group of the reactive tautomer ($k_{-1} \sim k_2$).



We also note that the carboxyl group in $\mathbf{1H}^+$ is likely to exist in a conformation that has the OH *synperiplanar* to the carbonyl in order to be stabilized by internal H-bonding with the methoxy oxygen as suggested by Stewart and Granger.¹⁴ In that array, the proton is not directly accessible

for transfer to solvent water. This suggests the possibility that C-C bond cleavage from 2H^+ could occur with an intramolecular proton transfer from the carboxyl group to the methoxy group (Scheme 5). Our results indicate that while this transition state (Figure 1) gives a CKIE (1.034) that is in better agreement with the observed CKIE, this pathway involves a barrier that is significantly higher in energy ($\Delta G^\ddagger = 46.4$ kcal/mol) than that involving the proton transfer to a solvent water molecule ($\Delta G^\ddagger = 23.7$ kcal/mol).⁸ From this analysis, we conclude that the reaction proceeds by intermolecular deprotonation of the carboxyl by the solvent water as was proposed previously.⁸

Scheme 5. An alternative high-energy pathway with transfer of the carboxyl proton to the adjacent ether oxygen (via $1'\text{H}^+$ and $2'\text{H}^+$) rather than to solvent.

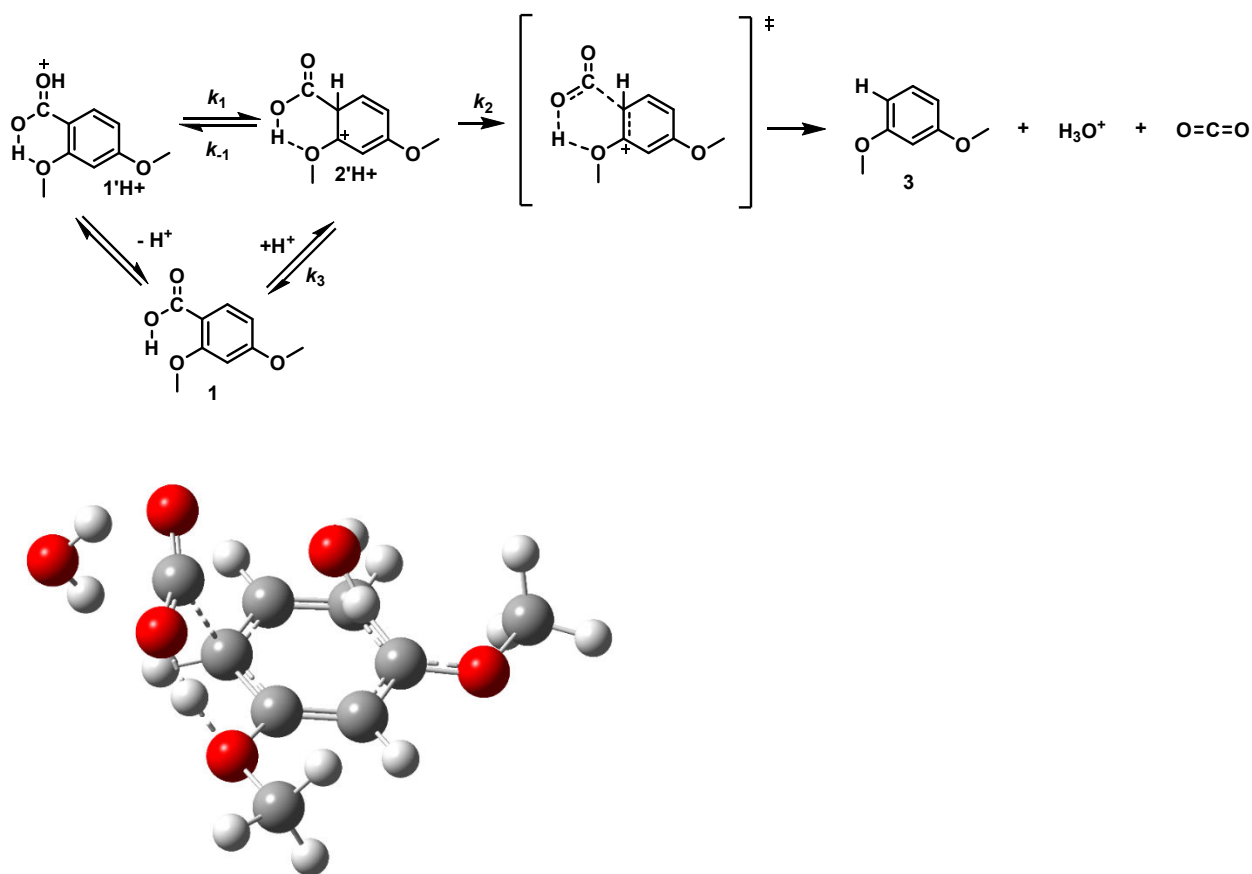
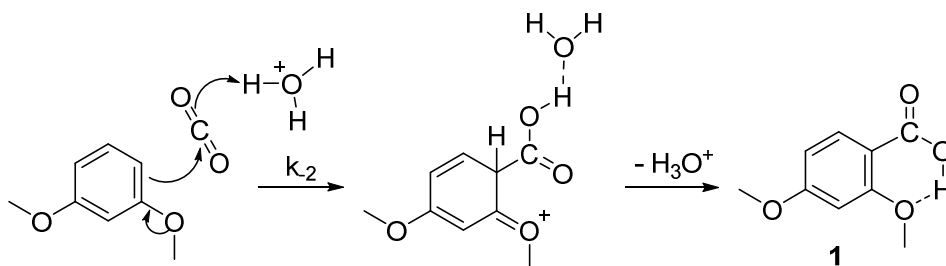


Figure 1. Calculated transition state for decarboxylation of the conjugate acid via internal transfer of the carboxyl proton to the methoxy group. This transition state is much higher in energy ($\Delta G^\ddagger = 46.4$ kcal/mol) than the alternative process shown in Scheme 4 ($\Delta G^\ddagger = 23.7$ kcal/mol).⁸

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An important conclusion from knowledge of the details of the mechanism of decarboxylation is the application to the reverse process using the principle of microscopic reversibility. That process would incorporate CO₂ into 1,3-dimethoxybenzene in acidic solutions to form 2,4-dimethoxybenzoic acid or an isomer of that species. Our results show that deprotonation of the carboxyl occurs ahead of C-C bond cleavage in a common step with imperfect synchronization. In the reverse, the substituted benzene ring undergoes addition to CO₂ to form a C-C bond at a benzene-derived carbon α to that of a methoxy group. This produces a positively charged carbon attached to the benzene ring that is stabilized by its oxonium ion character (Scheme 6). In that process, addition of a solvent proton to the oxygen from CO₂ occurs to a small extent. The unstable assembly is lowered in energy as the carboxyl group with its proton forms adjacent to a positive charge on the benzene ring”: Scheme 6 is written as the microscopic reverse of Scheme 4. Formation of the internal H-bond in **1** helps stabilize the final product from addition of CO₂.

Scheme 6. Acid catalyzed trapping of carbon dioxide



■ CONCLUSIONS

The rate of decarboxylation of the neutral form of **1** increases in acidic solutions, with the acidity dependence of the rate consistent with formation of a more reactive species (**2H⁺**) that is a minor tautomer of the conjugate acid of **1**. For the reaction in the dilute acid medium, the small CKIE is consistent with formation of the reactive tautomer by proton migration being rate determining. In more acidic solutions, the larger CKIE is consistent with C-C bond breaking being a significant part of the rate-determining step. That step avoids the formation of protonated CO₂ as the carboxyl proton transfers to water while the C-C bond breaks, producing CO₂. In addition, a proton transfer step that precedes the C-C bond-breaking step is also partially rate-determining.

■ EXPERIMENTAL SECTION

The decarboxylation reactions were carried out in 125 mL septum-capped bottles. Solutions of perchloric acid (50 mL) were added to the vessel and the headspace was purged with helium to remove atmospheric CO₂. The reactant, 2,4-dimethoxybenzoic acid (**1**, 0.1 mL), was dissolved in degassed dimethyl sulfoxide (0.5 mL) and injected directly into the vessel to initiate the reaction. The reaction vessels were maintained at 60°C by immersion in a thermostatic circulating water bath and cooled to 0 °C prior to analysis at the designated reaction time points. The headspace was sampled by use of a pressure-lock analytical syringe with a side-port taper needle. The reaction progress was approximated by reaction time and by comparison with the peak area obtained from mass intensity scans on an isotope-ratio mass spectrometer coupled to a gas chromatograph and combustion oven (GC-IRMS). Measurements of materials from complete-conversion of the reactants were taken after 24-96 hrs, based on the half-life of the reaction. The reaction sequence was repeated without substrate as a control experiment and CO₂ was not detected in the headspace. The magnitudes of k^{12}/k^{13} kinetic isotope effects (CKIE) were calculated based on the equation developed by Bothner-By and Bigeleisen²³ for monitoring kinetic isotope effects in decarboxylation reactions:²³ The term f refers to the fraction of the total conversion reaction that has occurred.

$$k^{12}/k^{13} = \log(1 - f) / \log[1 - f(N_x/N_{x0})]$$

k^{12} and k^{13} are the observed first-order rate coefficients for reaction of the isotopic materials. R and R_0 in the original equation are replaced with N_x and N_{x0} , the ¹³C/¹²C concentration ratios as determined and reported from the IRMS, converted into abundances: $N_x = C^{13}O_2/C^{12}O_2$ at $f=f$ and $N_{x0} = C^{13}O_2/C^{12}O_2$ at $f=1$.

Data collected to obtain the CKIE for decarboxylation of **1** are summarized in Table 2 including the resulting isotope effects.

Table 2. k^{12}/k^{13} kinetic isotope effects for the acid-catalyzed decarboxylation of 2,4-dimethoxybenzoic acid

[HClO ₄], wt %	<i>f</i>	<i>N_x</i>	<i>N_{x0}</i>	CKIE
42%	0.13	0.010498	0.010712	1.0213
	0.13	0.010498	0.010712	1.0212
	0.25	0.010497	0.010712	1.0225
	0.25	0.010500	0.010712	1.0221
	Av.			1.022 ±0.002
10%	0.13	0.010693	0.010710	1.0018
	0.13	0.010692	0.010710	1.0019
	0.25	0.010694	0.010710	1.0018
	0.25	0.010693	0.010710	1.0019
	Av.			1.002 ±0.002

Optimal geometries and the associated vibrational frequencies were calculated with M06-2X/6-311⁺⁺G(2d,2p) as implemented in Gaussian 09.²⁴ All calculations included two explicitly modelled water molecules and considered the bulk solvent implicitly with the SMD model. The calculated value for the intrinsic CKIE for the decarboxylation of **2H⁺** was obtained using ISOEFF 07.^{25,26}

■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Full citation for ref 24; coordinates and thermodynamics of optimized structures

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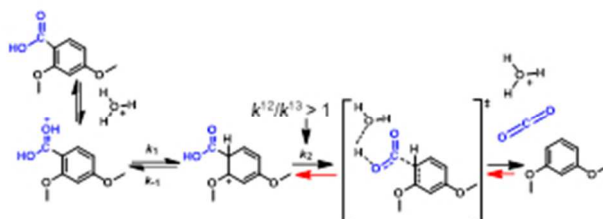
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Where the loss of CO₂ is acid catalyzed, the carbon isotope effect is significant but reduced. The reverse is acid catalyzed trapping of CO₂ with partially rate-determining carboxyl bond formation.

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