

HYDROTHERMAL DECARBOXYLATION OF RCO_2H STUDIED BY REAL-TIME VIBRATIONAL SPECTROSCOPY

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Water at high pressure and high temperature (the hydrothermal environment) is wide spread in the Earth's crust. On the ocean floor the high density of water leads to hot water "black smoker" vents which were first discovered in 1979 on the deep-sea Pacific rift zones.¹ Mineral-laden fluid H_2O flows at temperatures of about 350°C under pressures determined by hydrostatics, e.g. 270 atm at a depth of 2500 meters.^{2,3} At these conditions, H_2O maintains a single fluid phase. A large amount of organic chemical synthesis occurs in the shear layer where the hot vent water interfaces with the cooler sea water.⁴ These unusual conditions thermodynamically drive alterations of relatively simple, but universally important molecules such as H_2 , CO , CO_2 , H_2S , NH_3 , CH_4 and H_2O , to synthesize larger molecules,⁵⁻⁷ such as various carboxylic acids,^{6,8,10} amino acids,⁶ aldehydes¹¹ and metal carboxylate complexes¹². Feeding on the resulting organic compounds, a complex ecosystem ranging from single cell species to large invertebrates develops in the vicinity of these vents¹³⁻¹⁵ and, thus, the synthesis of small organic molecules in the hydrothermal regime is thought to have contributed to the origin of life.^{14,16,17}

Underlying these fascinating and profound issues is a series of basic questions in thermodynamics and kinetics. A large body of measurements and analyses in the references cited above particularly support the notion that thermodynamics is the main driving force for the synthesis of small organic molecules in the hydrothermal environment. On the other hand, it appears that, by comparison, relatively few kinetic considerations have been incorporated into reactions of small organic and inorganic molecules under conditions particular to hydrothermal vents. Instead, most hydrothermal and supercritical water kinetic measurements and analyses have been driven by biomass conversion¹⁸⁻²¹ and waste stream remediation technologies.²²

Hydrothermal vents involve transient phenomena in which temperature gradients exist in the shear layer and where turbulent mixing occurs. As such, kinetic phenomena are likely to be very important factors. The vast majority of kinetic and mechanistic studies of alterations of organic compounds in the hydrothermal medium are based on analysis of products after cooling a tube reactor that was heated in the batch mode or by post-reaction analysis of products from a flow reactor. Comparatively fewer kinetic and mechanism data have been obtained spectroscopically during the reaction, especially in the flow mode.²³⁻³⁴ This method, however, provides an unprecedented level of detail about hydrothermal chemical reactions.

The focus of this talk is on recent work dealing with the kinetics and mechanism of decarboxylation of carboxylic acids in real-time at hydrothermal conditions.^{30,33,34} Such studies augment previous work on kinetics conducted by other experimental methods.^{10,35}

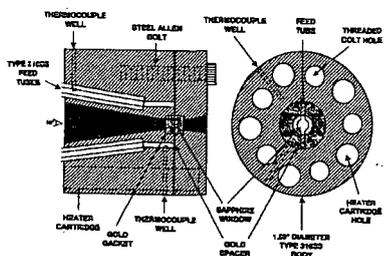


Fig. 1. The flow cell used for real-time IR at hydrothermal conditions.

The experimental methods used in this work are described elsewhere in detail.^{25,27,32} The short-path length IR flow cell is shown in Fig. 1 and is connected to a flow control apparatus that precisely maintains the temperature ($\pm 1^\circ\text{C}$), pressure (± 1 atm) and flow rate (0.01 - 1 ml/min). The resulting residence times in kinetic regime studied are 1-60 sec. These devices enabled a variety of kinetic and mechanistic details to be uncovered that would be opaque in the batch mode where determinations are made at longer times and by post-reaction analyses.

Wall-Assisted Decarboxylation. The clearest evidence that the reactor surface could assist or catalyze the decarboxylation reaction was obtained with formic acid, HCO_2H .³³ Figure 2 shows the rate of formation of CO_2 from a 1.00 *m* HCO_2H solution as a single phase at 310°C . Two batches of 316 stainless steel (SS) gave somewhat different results but, at least initially, not much different from 90/10 Pt/Ir. Titanium gave a much slower rate of CO_2 formation. These results strongly suggest that the reactor wall can affect the rate of decarboxylation of HCO_2H .

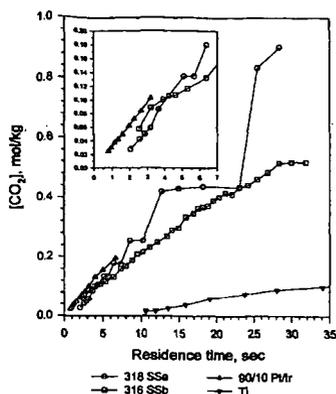


Fig. 2. The concentration of CO_2 from decomposition of $1.00 \text{ m HCO}_2\text{H}$ at 310°C and 275 atm as a function of residence time in four types of cell materials.

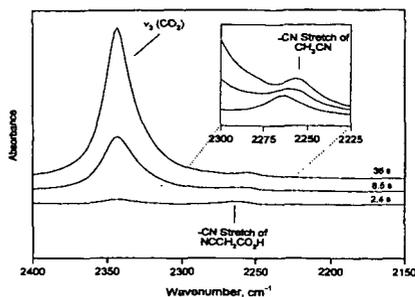


Fig. 3. A time series of IR spectra for $1.00 \text{ m NCCH}_2\text{CO}_2\text{H}$ at 220°C under 275 atm in the 316 SS flowcell. Conversion by reaction (1) is indicated.

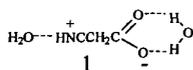
Homogeneous Phase Decarboxylations. The mechanisms of hydrothermal reactions of organic compounds in H_2O solution can be expected to depend on the functional groups attached to the reactive site. This subject has not been investigated previously and was established by the use of the SS and Ti cells in Fig. 1 and with another higher volume cell by Raman spectroscopy.^{30,34} Derivatives of acetic acid were used for this work RCO_2H ($\text{R} = \text{CCl}_3^-$, CF_3^- , CF_3CH_2^- , $\text{HOC}(\text{O})\text{CH}_2-\text{NH}_2\text{C}(\text{O})\text{CH}_2-$, NCCH_2- , and $\text{CH}_3\text{C}(\text{O})-$). All of these substituents are electron-withdrawing which accelerates the decarboxylation reaction. Relatively small effects were induced by the material of construction (SS or Ti) of the cell. The R group on the other hand exerted a pronounced effect on the rate of decarboxylation, which is described at least initially by reaction 1. Figure 3 illustrates



reaction 1 when $\text{R} = \text{NCCH}_2-$ in which the reactant $-\text{CN}$ stretch, product $-\text{CN}$ stretch (CH_3CN), and CO_2 can all be spectrally observed simultaneously. The spectral absorbance can be integrated to obtain the concentrations at all times. Figure 4 is a first-order rate plot for the decarboxylation of $\text{NCCH}_2\text{CO}_2\text{H}$ at 275 atm and the temperatures shown. These data can, of course, be expressed in the Arrhenius form.³⁴ When kinetic constants of this type are determined for all of the substituted acetic acids, the rates or Arrhenius parameters failed to correlate with common linear free energy relations, such as the electronic Hammett or Taft parameters.³⁶ On the other hand, the use of the expanded Taft equation 2 produced useful results. Equation 2 expresses the steric, E_s , and electronic, σ^* , substituent parameters weighted by the adjustable variables ρ and δ in terms of the rate constants, k , normalized to that of acetic acid, k_0 , measured at the same conditions. Figure 5 shows that these categories of compounds separate. The line shown represents the fit for $\rho = 1.5$ and $\delta = -3.6$. The

$$\ln(k/k_0) = \delta E_s + \rho \sigma^* \quad (2)$$

larger absolute value of δ indicates that the steric effect of R is somewhat more important in the rate than the electronic effect. This finding is consistent with structure 1 in which H_2O polarizes the carboxylate group, rather than structure 2 in which H_2O acts as a nucleophile, because the steric bulk of R should impede the reaction in the latter case.



Another category of compounds in Fig. 5 arises when $\text{R} = \text{HOC}(\text{O})\text{CH}_2-$ and $\text{NH}_2\text{C}(\text{O})\text{CH}_2-$. These compounds react faster than expected and probably do so as a result of their ability to form the cyclic transition state structure 3. This structure facilitates the unimolecular pathway of decarboxylation. When $\text{R} = \text{CF}_3-$, Fig. 5 shows the rate of decarboxylation is slower than expected from the substituent effect. The CF_3- group impedes the process probably because the hyperconjugative interaction shown in structure 4 strengthens the C-C bond.

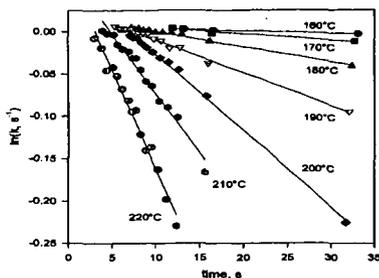


Fig. 4. First-order rate plot of decarboxylation of $\text{NCCH}_2\text{CO}_2\text{H}$ at 275 atm.

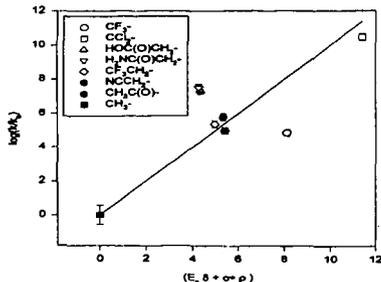
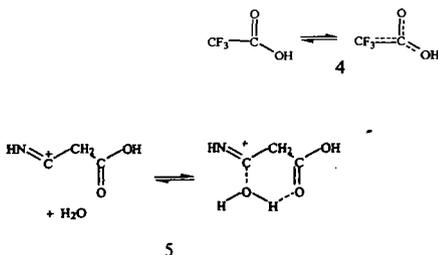
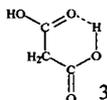


Fig. 5. A Taft plot for decarboxylation of RCO_2H at 200°C and 275 atm.



The Effect of pH. Strecker synthesis is believed to provide easy access to α -amino and α -hydroxyl carboxylic acids in the early life forming process.³⁷ In this reaction, NH_3 and HCN react with aldehydes and ketones to form the α -amino and α -hydroxy organonitriles that react with H_2O to form the carboxylic acid. Our study of $\text{NCCH}_2\text{CO}_2\text{H}$ ³⁴ decarboxylation raised a question about the conditions by which H_2O reacts with the $-\text{CN}$ group. To this end, the kinetics of decomposition of $\text{NCCH}_2\text{CO}_2\text{H}$ in 0.3-1.0N HCl was conducted at 150-260°C under 275 atm pressure. The mechanism worked out is shown in Fig. 6. Channel A occurs in the absence of acid as is discussed above. Channels B, C and D are opened by the presence of HCl and channel A does not occur. Hence, the presence of acid makes the $-\text{CN}$ group more reactive than the $-\text{CO}_2\text{H}$ group while the reverse is true in neutral solution. The probable reason is that the $-\text{CN}$ group is protonated by acid which facilitates nucleophilic attack by H_2O as shown in structure 5.

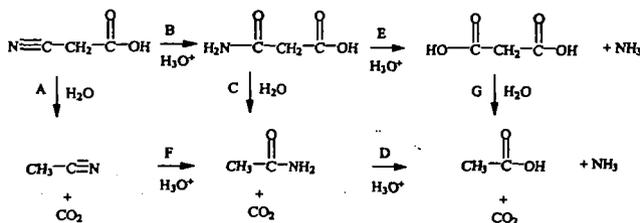


Fig. 6. The pathway of decarboxylation and deamination of $\text{NCCH}_2\text{CO}_2\text{H}$ determined in the hydrothermal regime.

In conclusion, real-time IR and Raman spectroscopy during hydrothermal reactions provides experimentally-based, mechanistic details about hydrothermal reactions under conditions of interest in geothermal vents and in waste steam remediation. Several different types of molecule-dependent decarboxylation mechanisms are uncovered for the seemingly simple reaction 1. In some cases H_2O appears to play a key role whereas in others it does not.

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