

# Correction to “Organic Acids Tunably Catalyze Carbonic Acid Decomposition”

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In our recent paper on the gas-phase decomposition of carbonic acid, incorrect conformations of some of the free monocarboxylic acids were used for calculating the reactant energies in the acid-catalyzed reaction, which introduced an error

of  $\sim 4.0$  kcal/mol in some of the calculated data. Here, we correct that error. The corrected entries of Table 1 are provided here along with amended Figures 3–5.

These changes also modify some of the conclusions: (1) the monosubstituted carboxylic acids are always better catalysts than the unsubstituted one, formic acid (Table 1). Moreover, while the carboxylic acids still exhibit linear correlations between the reaction free-energy barrier and the acid  $pK_a$ , the relationship differs between acids with electron-withdrawing groups (e.g., chlorinated substituents) and electron-releasing groups (e.g., alkyl substituents); see Figure 4. The same appears to be true of the Hammett correlation (Figure 5).

Finally, the estimated effective rate constant for the formic acid-catalyzed decomposition, accounting for atmospheric concentrations of the acid, is  $k_{\text{HCOOH}}^{\text{eff}}(T) = 8.0 \times 10^{-6} \text{ s}^{-1}$ , which, while smaller than that estimated in the original paper, is still an order of magnitude faster than for the water-catalyzed reaction,  $k_{\text{H}_2\text{O}}^{\text{eff}}(T) = 8.0 \times 10^{-7} \text{ s}^{-1}$ .

## ■ ACKNOWLEDGMENTS

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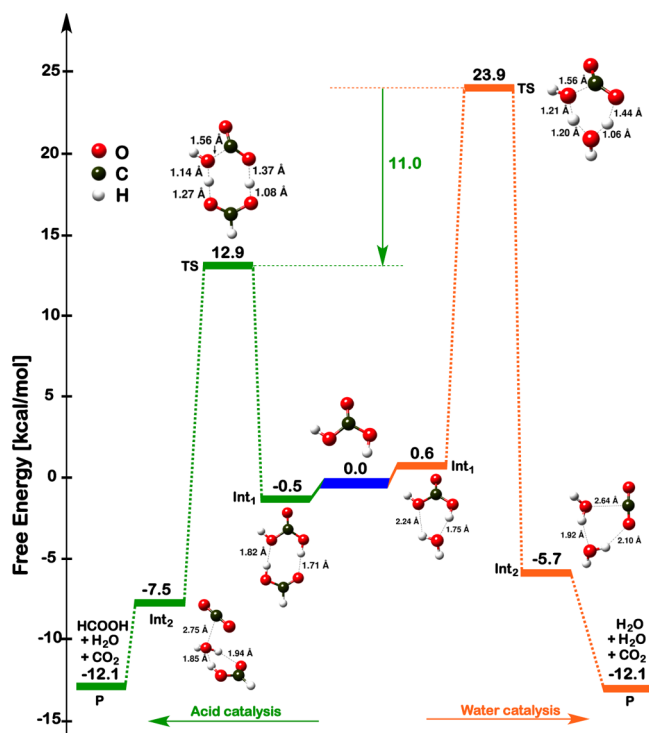


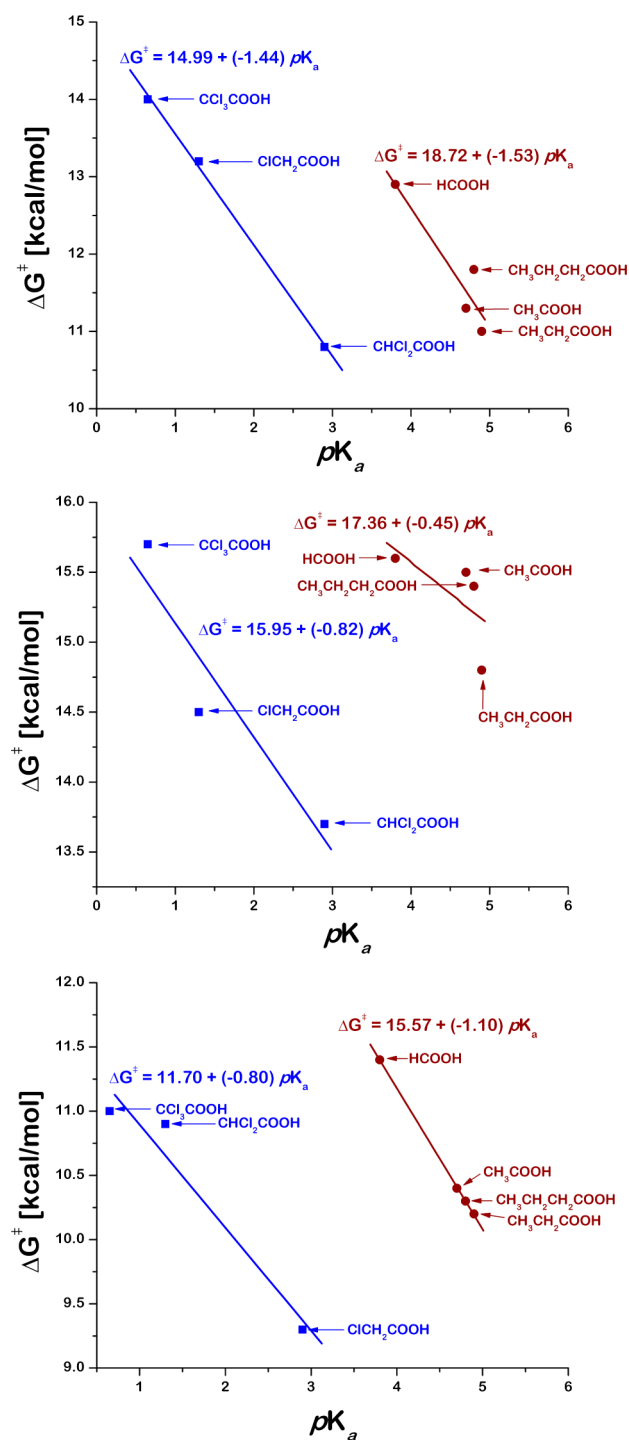
Figure 3. Calculated free-energy profile (298.15 K, 1 atm) of formic acid-catalyzed (left) and water-catalyzed (right) gas-phase decomposition of  $\text{H}_2\text{CO}_3$ .

Table 1. M06-2X/aug-cc-pVTZ Calculated Zero Point-Corrected Energies,  $\Delta E$ , and Free Energies,  $\Delta G$ , (in kcal/mol) of Various Species Involved in the Uncatalyzed and Catalyzed Gas-Phase Decomposition of a  $\text{H}_2\text{CO}_3$  Molecule<sup>a</sup>

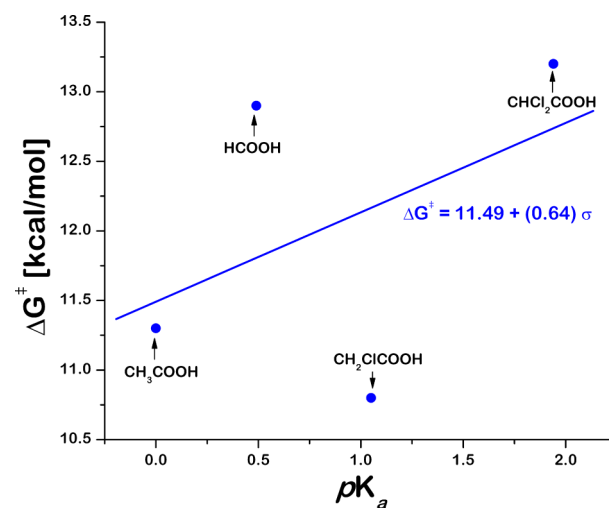
catalyst	Int <sub>1</sub>		TS		Int <sub>2</sub>		P	
	$\Delta E$	$\Delta G$	$\Delta E$	$\Delta G$	$\Delta E$	$\Delta G$	$\Delta E$	$\Delta G$
formic acid	−10.8	−0.5	1.6	12.9	−15.5	−7.5	−4.4	−12.1
acetic acid	−12.0	−1.9	0.3	11.3	−15.7	−7.2	−4.4	−12.1
monochloroacetic acid	−11.7	−2.3	0.3	10.8	−16.8	−10.6	−4.4	−12.1
dichloroacetic acid	−10.2	0.2	1.7	13.2	−16.0	−6.5	−4.4	−12.1
trichloroacetic acid	−10.4	0.0	2.0	14.0	−16.3	−7.8	−4.4	−12.1
propionic acid	−13.1	−2.2	−0.8	11.0	−16.9	−8.7	−4.4	−12.1
butyric acid	−12.8	−1.5	−0.4	11.8	−16.6	−6.7	−4.4	−12.1

<sup>a</sup>Energies are reported with respect to the separated reactants.

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**Figure 4.** Calculated reaction free-energy barriers versus  $pK_a$  for the acid-catalyzed  $H_2CO_3$  decomposition (top panel), tautomerization of vinyl alcohol, (middle panel), and isomerization of a methoxy radical (bottom panel).



**Figure 5.** Calculated Hammett correlation between the reaction free-energy barriers of the acid-catalyzed  $H_2CO_3$  decomposition and  $\sigma$ -values of the acids.