



Short communication

Reversibility of the catalytic ketonization of carboxylic acids and of beta-keto acids decarboxylation

Alexey V. Ignatchenko*, Andrew J. Cohen

Chemistry Department, St. John Fisher College, 3690 East Avenue, Rochester, NY 14618, United States

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QTBSBXVTEAMEQO-UHFFFAOYSA-N
CSCPPACGZOOOGX-UHFFFAOYSA-N MIPK:
SYBYTAAJFKOIEJ-UHFFFAOYSA-N DIPK:
HXVNBWAKAOHACI-UHFFFAOYSA-N
KQNPFTWMSNSAP-UHFFFAOYSA-N CO2:
CURLTUGMZLYLDI-UHFFFAOYSA-N

ABSTRACT

Decarboxylation of beta-keto acids in enzymatic and heterogeneous catalysis has been considered in the literature as an irreversible reaction due to a large positive entropy change. We report here experimental evidence for its reversibility in heterogeneous catalysis by solid metal oxide(s) surfaces. Ketones and carboxylic acids having ^{13}C -labeled carbonyl group undergo $^{13}\text{C}/^{12}\text{C}$ exchange when heated in an autoclave in the presence of $^{12}\text{CO}_2$ and ZrO_2 catalyst. In the case of ketones, the carbonyl group exchange with CO_2 serves as evidence for the reversibility of all steps of the catalytic mechanism of carboxylic acids ketonic decarboxylation, i.e. enolization, condensation, dehydration and decarboxylation.

1. Introduction

Chemical processes with CO_2 release or capture are receiving ever increasing attention in connection with disturbances of the global carbon dioxide cycle. The mechanism of one of these enzymatic reactions, the stepwise vs. the concerted decarboxylation of beta-keto acids, has been debated since the beginning of the twentieth century [1–8]. This remarkably enlightening and still evolving discussion is about making careful choices of appropriate experimental and computational methods for mechanistic studies in atypical cases.

The mechanism of another reaction important for the production of renewable biofuels, the catalytic decarboxylative ketonization of carboxylic acids, may incorporate the above beta-keto acids decarboxylation step on surface of metal oxide catalysts [9–12]. Conclusions made in the literature on beta-keto acids behavior in solutions may well be applicable to the decarboxylation on surfaces during the catalytic production of ketones from carboxylic acids.

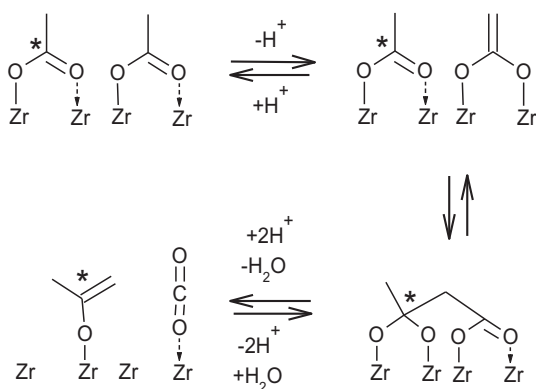
It is generally accepted that decarboxylative ketonization mechanism proceeds through enolization of one of the acid molecules on the surface of metal oxides followed by the condensation with the second one according to Scheme 1 [10–12]. By analogy with the aldol and Claisen condensations, we suggested to call these molecules the

enolic and carbonyl components [13]. Variations in the literature describe the carbonyl component (electrophile) as an acyl cation [10], a monodentate carboxylate [11] or a bidentate one [12], which may depend on the type of the metal oxide catalyst surface. The intermediate resulting from the condensation dehydrates to the beta-keto acid derivative [12], which decarboxylates to the enolic form of the final ketone product.

Recently, it has been suggested by Kluger [7] that decarboxylation of beta-keto acids in solutions or by enzymes might be reversible and that an important role of enzymes is to provide conditions for effectively removing CO_2 away from the enolized ketone product, slowing down the reverse reaction. However, the reversibility of beta-keto acids decarboxylation has neither been demonstrated experimentally for enzymatic reactions, nor in the heterogeneous catalysis. We are reporting experimental results demonstrating for the first time the reversibility of the catalytic decarboxylative ketonization reaction, which presumably proceeds through the formation of beta-keto acids.

This finding implies not only the reversibility of beta-keto acids decarboxylation but also reversibility of their formation in the condensation step, as well as all other steps outlined in Scheme 1, so that the overall catalytic reaction of carboxylic acids to ketones on metal oxides is reversible, while ketones remain thermodynamically favored

* Corresponding author at: Basil Hall, St. John Fisher College, 3690 East Avenue, Rochester, United States.
E-mail address: alexey.ignatchenko@gmail.com (A.V. Ignatchenko).



Scheme 1. Mechanism of $^{13}\text{C}/^{12}\text{C}$ exchange between ketones and CO_2 resulting from reverse decarboxylative ketonization reaction. (Although the strongest adsorption of CO_2 on metal oxides is realized through formation of surface carbonates, the weakly adsorbed linear form of CO_2 shown here is designed to illustrate preparedness for the exchange step with the gas phase CO_2).

products.

2. Experimental

All experiments have been conducted inside a 22 mL volume non stirred autoclave which allows small amounts of isotopically labeled compounds to be used on a milligram scale. Liquid compounds were loaded on the bottom of the autoclave. The amount of CO_2 was controlled by adding weighed pieces of dry ice and immediately sealing the autoclave. Pieces of catalyst were mounted in the top compartment of the autoclave so that only vapors can reach it and react. At the end of the specified reaction time (Table 1), the autoclave was chilled and the liquid products were collected from the bottom for the gas chromatography / mass spectroscopy (GC/MS) analysis. The degree of exchange was calculated as the fraction of the light isotopologue found in the labeled compounds at the end of the exchange reaction and corrected for the initial 99% ^{13}C isotopic purity of reagents and for the natural 1.1% occurrence of ^{13}C per carbon atom in CO_2 according to Eqs. A1 and A2 provided in Supplementary Material.

3. Results and discussion

If the reaction is taken in the reverse direction, starting from ketone,

Table 1
 $^{13}\text{C}/^{12}\text{C}$ exchange between carbonyl group of acids (ketones) and CO_2 in the presence of water with zirconia catalysts in 22 mL pressurized autoclave.

Entry #	Acid (ketone)	Amount, mg	Molar ratio, carbonyl: water: CO_2	Catalyst	Catalyst amount, mg	Time, hr	Temperature, °C	Measured degree of exchange (conversion)	Degree of exchange expected at full equilibrium	Rate, mmol/h	TOF, $\times 10^{-3} \text{ s}^{-1}$	Average TOF, $\times 10^{-3} \text{ s}^{-1}$
1	Isobutyric- ^{13}C	40	1: 23: 23	ZK	167.7	15	280	78.3%	94.8%	0.141	0.250	0.206
2	Isobutyric- ^{13}C	42	1: 21: 21	ZK	167.7	16.5	270	52.6%	94.5%	0.091	0.161	
3	Isobutyric- ^{13}C	39	1: 23: 23	ZR	155.2	17.3	280	55.6%	94.8%	0.092	0.163	0.142
4	Isobutyric- ^{13}C	41	1: 22: 22	ZR	155.2	16.5	280	37.4%	94.6%	0.068	0.121	
5	Acetic- ^{13}C	39	1: 16: 15	ZK	144	6	270	59.6%	92.8%	0.449	0.798	0.713
6	Acetic- ^{13}C	42	1: 15: 15	ZK	144	5	270	36.4%	92.8%	0.354	0.629	
7	Acetic- ^{13}C	41	1: 15: 15	ZR	124.2	5	270	16.2%	92.8%	0.178	0.316	0.334
8	Acetic- ^{13}C	38	1: 17: 16	ZR	124.2	6	270	23.2%	93.1%	0.198	0.351	
9	(Acetone-2- ^{13}C)	50	1: 12: 12	ZR	123.7	24	270	17.2%	91.4%	0.050	0.089	0.095
10	(Acetone-2- ^{13}C)	49	1: 13: 13	ZR	123.7	24	280	20.2%	91.9%	0.058	0.102	
11	MIPK ^a	430	1: 10:10	ZR	128	48	300	2.1%	–	0.017	0.028	0.027
12	MIPK ^a	430	1: 10:10	ZR	128	168	300	6.9%	–	0.016	0.027	
13	For comparison: Acetic + isobutyric acid making MIPK	600 + 880	1:2.5:2.5	ZR	124.0	120	300	39.5%	–	0.531	0.885	

^a Measured as the rate of disproportionation to acetone and DIPK, mediated by condensation with CO_2 .

water and CO_2 on the right hand side (Scheme 1), it could produce two molecules of carboxylic acids on the left hand side of the equation. Normally, this is not observed experimentally, because thermodynamic equilibrium favors the ketone product formation (calculations are provided in Supplementary Material). When we used ^{13}C label on the carbonyl group of the ketone in the autoclave reaction with CO_2 and water, the label was scrambled between the carbonyl group of the ketone and CO_2 . We propose that the scrambling takes place between two acetic acid molecules at the stage of their formation, while either one of the acids can go through the enolization process with equal probability on the path back to the ketone and CO_2 . It is the enolized acid which is losing CO_2 , while the carbonyl group of the other acid is used to regenerate the ketone. This observation serves as strong evidence for the reversibility of the catalytic decarboxylative ketonization of carboxylic acids, including all steps of the literature mechanism [12] with the consequence of affecting the reaction kinetic scheme.

It is less likely that $^{13}\text{C}/^{12}\text{C}$ exchange can proceed through some kind of a direct alkyl group transfer from ketone to CO_2 as in the concerted mechanism of ketonic decarboxylation, or via formation of alkyl radicals, or alkyl anions, given that all such options have been ruled out over the century-long debate in favor of the stepwise mechanism of alkyl group transfer via beta-keto acid formation [10–12]. The most recent experimental evidence against direct alkyl group transfer is that reported in the work of Oliver-Tomas et al. [14].

^{13}C -labeled carboxylic acids too exchange their carboxyl group presumably through the condensation between enolized surface carboxylate with CO_2 into intermediate malonic acid (Scheme 2, Table 1). Exchange via retro-Koch – Koch reaction equilibrium under chosen conditions is very unlikely. Retro-Koch decomposition of carboxylic acids requires much higher temperatures, above 500 °C, and cannot compete with the ketonic decarboxylation favored at 300 °C [14]. Only acids lacking alpha-hydrogens and not able to undergo ketonic decarboxylation may be forced into the retro-Koch reaction at extreme temperatures. Pivalic acid decomposition into isobutene and CO is an example described on zirconia catalyst at 550 °C [14]. Of the two acids studied in the present exchange experiments (Table 1), only isobutyric acid can theoretically decompose into alkene and CO by the unfavorable path, but acetic acid cannot do so. It would form rather inert methane, which does not convert back to AcOH on zirconia. An additional exchange would be required between CO and CO_2 by the water-gas shift reaction, which is also unlikely at temperatures below 300 °C. Neither CO, nor H_2 were detected by GC analysis of the vented gas.

Under these conditions, inside the non-stirred autoclave, and at

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