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Abstract

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REVERSIBILITY OF THE CATALYTIC KETONIZATION OF CARBOXYLIC ACIDS AND OF BETA-KETO ACIDS DECARBOXYLATION

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Abstract

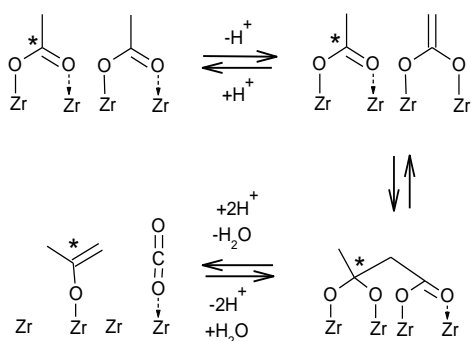
Decarboxylation of beta-keto acids in enzymatic and heterogeneous catalysis has been considered in the literature as an irreversible reaction due to a large positive entropy change. We report here experimental evidence for its reversibility in heterogeneous catalysis by solid metal oxide(s) surfaces. 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.

KEYWORDS: Reaction mechanism; zirconia catalyst; carbon dioxide; decarboxylative ketonization; ketonic decarboxylation; reaction equilibrium.

1. INTRODUCTION

Chemical processes with CO₂ 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.



Scheme 1. Mechanism of ¹³C/¹²C exchange between ketones and CO₂ resulting from reverse decarboxylative ketonization reaction.¹

¹ Although the strongest adsorption of CO₂ on metal oxides is realized through formation of surface carbonates, the weakly adsorbed linear form of CO₂ shown here is designed to illustrate preparedness for the exchange step with the gas phase CO₂.

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 CO₂ 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 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 CO₂ 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 labelled compounds at the end of the exchange reaction and corrected for the initial 99% ¹³C isotopic purity of reagents and for the natural 1.1% occurrence of ¹³C per carbon atom in CO₂ according to equations A1 and A2 provided in Supplementary Material.

3. RESULTS AND DISCUSSION

If the reaction is taken in the reverse direction, starting from ketone, water and CO₂ 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 ¹³C label on the carbonyl group of the ketone in the autoclave reaction with CO₂ and water, the label was scrambled between the carbonyl group of the ketone and CO₂. 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 CO₂. It is the enolized acid which is losing CO₂, 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 ¹³C/¹²C exchange can proceed through some kind of a direct alkyl group transfer from ketone to CO₂ 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].

¹³C-labeled carboxylic acids too exchange their carboxyl group presumably through the condensation between enolized surface carboxylate with CO₂ 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 CO₂ by the water-gas shift reaction, which is also unlikely at temperatures below 300 °C. Neither CO, nor H₂ were detected by GC analysis of the vented gas.

Under these conditions, inside the non-stirred autoclave, and at relatively low temperatures 270-280 °C, the reaction is much slower in comparison to a continuous gas flow reactor typically operating at higher temperatures, 350-450 °C. As a reference point, we have tested the rate of the cross-ketone formation from a mixture of acetic and isobutyric acids under exactly the same conditions. The turnover frequencies (Fig. 1, Table 1) have been calculated on the basis of the computational modelling which describes each catalytic site as constructed out of four zirconium atoms [12] and by using the BET surface areas measured for the employed zirconium oxide catalysts.

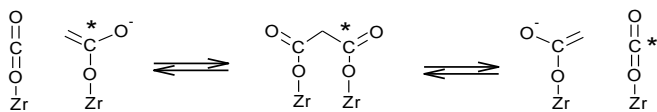
Reactions under the chosen conditions might be limited by diffusion. Typical reaction rates of the catalytic conversion of carboxylic acids to ketones with the same catalyst in the continuous flow reactor at higher temperatures are usually much higher, up to three orders of magnitude. It can be seen from Fig. 1 that the rate of ¹³C/¹²C exchange between carbonyl groups and CO₂ is only slightly lower compared to the decarboxylative ketonization rate. If the same ratio of the forward and the reverse decarboxylative ketonization reaction in the autoclave is maintained for the continuous process under comparable partial pressure of CO₂, it will signify a substantial inhibition of the reaction rates by CO₂ in commercial processes, which has not been recognized yet.

Previously, it was believed that such inhibition is due to the adsorption of products, CO₂, water and ketones, competing with adsorption of reagents on the catalytic sites. Evidently, the reverse reaction can make its own and even more important contribution to the inhibition of the decarboxylative ketonization reaction.

A typical industrial reactor employed for the production of ketones might have 60 - 90 psi pressure, an order of magnitude lower compared to the 600 psi estimated pressure in our experiments, so that the rate of ketones condensation with CO₂ will be lower. However, newly developing technologies for the conversion of biomass to fuels by the decarboxylative ketonization under supercritical water conditions require high pressures [15], so the inhibition of the reaction rate by CO₂ could become significant.

KOH treated catalyst (ZK) showed somewhat higher activity for the ¹³C/¹²C exchange (Fig. 1) in line with its generally higher activity for the decarboxylative ketonization reaction [16,17]. Higher exchange rates might be attributed to a higher adsorption of CO₂ on the alkaline metal promoted surface.

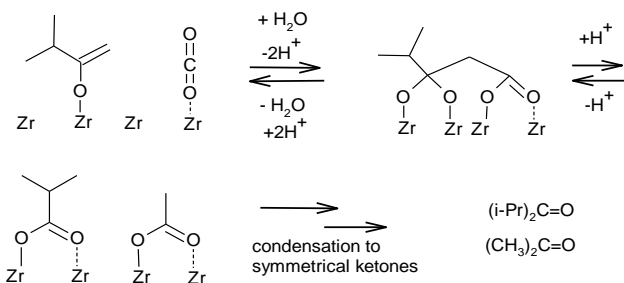
We have found that acetic acid is more active for the exchange reaction compared to isobutyric acid at the same molar concentration of acids in the reactor. One possible explanation is the lower boiling point and higher concentration of acetic acid in the vapor phase. Another factor is the lower degree of branching at the alpha position of acetic acid, so its condensation with CO₂ after enolization proceeds faster. This is in agreement with the computational data showing that the condensation with carboxylic acids is also faster for the enolized acetate vs. isobutyrate [12].



Scheme 2. Mechanism of ¹³C/¹²C exchange between carboxylic acids and CO₂ as a result of the reversible condensation - decarboxylation reaction.¹

Ketones represented by acetone and 3-methylbutan-2-one (methyl isopropyl ketone - MIPK), react slower in $^{13}\text{C}/^{12}\text{C}$ exchange compared to acids (Fig. 1). In general, ketones adsorption on metal oxides is weaker [10–12], which may explain their lower activity. In addition, the path for the $^{13}\text{C}/^{12}\text{C}$ exchange for carboxylic acids is shorter (Scheme 2), while ketones have to go through more steps (Scheme 1). The observed difference in reaction rates for ketones and carboxylic acids is in agreement with the kinetic relevance of the enolization and condensation of carboxylic acids in the mechanism of the decarboxylative ketonization. Combination of these steps was proposed to be limiting the whole mechanism [11,12]. These steps are also part of the $^{13}\text{C}/^{12}\text{C}$ exchange mechanism for ketones with CO_2 , but not for the exchange of carboxylic acids with CO_2 . Thus, all factors promote faster exchange for carboxylic acids compared to ketones.

Particularly interesting is the disproportionation of the cross-ketone, MIPK, to the symmetrical ketones, acetone and di-isopropyl ketone (DIPK), induced by the presence of CO_2 and water (Scheme 3). Regardless of which side of MIPK, either iso-propyl or methyl group, is undergoing enolization and condensation with CO_2 , the same two acids, isobutyric and acetic, can be produced after hydration and retro-condensation steps. Unlike the case of acetone exchange reaction, in which two molecules of acetic acid are produced and which can go back only to acetone, pair of isobutyric and acetic acids do not just go back to MIPK, but also yield two respective symmetrical ketones. Activity of unlabeled MIPK for the carbonyl group exchange (Fig. 1, Table 1) can only be seen through the formation of those two symmetrical ketones, while the intermediate path back to the starting cross-ketone cannot be detected. Therefore, activity of unlabeled MIPK appears about twice lower compared to the intrinsic value.



Scheme 3. Mechanism of MIPK disproportionation to acetone and DIPK in the presence of CO₂ and water.¹

Similarly, a mixture of two symmetrical ketones, acetone and DIPK, has produced detectable traces of the cross-ketone, MIPK, under similar conditions. The degree of conversion was not measured due to the low amount of MIPK produced. The value of the equilibrium constant, $K_{eq} = 12.5$, calculated at 300 °C favors acetone and DIPK, 92.6% fraction, vs. MIPK, 7.4% fraction (for details, see Supplementary Material). It is in agreement with the fact that the selectivity to the cross-ketone vs. symmetrical ketones is below statistically expected value with zirconia catalyst [12,17].

Discovery of the side reaction which converts the cross ketone into two symmetrical ketones opens a possibility for a partial thermodynamic control over the cross-selectivity in the decarboxylative ketonization of a mixture of carboxylic acids in a competition with the kinetic control [17].

A non-catalytic version of the exchange reaction between labeled and non-labeled carboxyl groups has been noticed first in 1959 by Nakai et al. [18] during their study of the cross-ketone formation by the pyrolysis of sodium salts of a mixture of two carboxylic acids. Remarkably, even after a short time and incomplete conversion, carboxylic groups of both

unreacted acids already become labeled, thus, indicating carboxyl exchange between acids at temperatures in the 310-320 °C and 350-360 °C range. The results were erroneously interpreted in support of a radical mechanism of the decarboxylative ketonization due to the next flaw in data analysis. When pyrolysis of the non-labeled phenylacetic acid to the respective ketone was done in the presence of $\text{Na}_2^{14}\text{CO}_3$ at 240-250 °C, there was no $^{14}\text{C}/^{12}\text{C}$ exchange detected. The fact that both the unreacted acid and the ketone did not acquire ^{14}C label from sodium carbonate was used to support radical mechanism. However, all other exchanges between labeled and non-labeled acids took place only at higher temperatures, above 310 °C. At lower temperatures, 240-260 °C, not only there were no exchange between acid and sodium carbonate, but the same pairs of labeled and non-labeled acids also did not exchange. Thus, it is not clear whether the exchange between sodium carbonate and acids at lower temperatures was just too slow and, for that reason, was undetected.

Carboxylic group exchange between pairs of acids prior to their ketonization has been also described in several follow-up studies of the pyrolysis of salts with the carboxylic group labeled on one of the acids [19,20], but none of those studies have interpreted this information in support of the currently most accepted mechanism through beta keto acids formation. This exchange is completely missing in all of the recent reviews on the mechanism of the decarboxylative ketonization reaction.

4. CONCLUSIONS

In conclusion, carboxyl exchange between two acids, or a ketone and CO₂, or a carboxylic acid and CO₂ takes place during the catalytic conversion of carboxylic acids into ketones according to the most accepted mechanism of ketonic decarboxylation (Schemes 1-3). It is mediated by the condensation of CO₂ as the electrophile with the enolized form of a ketone or a carboxylic acid as the nucleophile. The exchange process becomes possible when the condensation is followed by the retro-condensation. In the case of ketones, the exchange proceeds through the formation of a beta keto acid in reverse to its decarboxylation. Disproportionation of the unsymmetrical ketone leads to the formation of two symmetrical ketones.

ACKNOWLEDGMENTS

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Appendix A. Supplementary Material: Catalyst preparation, experimental details, product analysis, calculation of equilibrium constants.

FIGURE CAPTIONS

Fig. 1. Turnover frequencies for the $^{13}\text{C}/^{12}\text{C}$ exchange of CO_2 with the labeled carbonyl group of ketones and carboxylic acids in comparison to the cross-ketonization of acetic and isobutyric acids catalyzed by untreated (ZR) and KOH treated (ZK) ZrO_2 catalysts.

SCHEME TITLES

Scheme 1. Mechanism of $^{13}\text{C}/^{12}\text{C}$ exchange between ketones and CO_2 resulting from reverse decarboxylative ketonization reaction.

Scheme 2. Mechanism of $^{13}\text{C}/^{12}\text{C}$ exchange between carboxylic acids and CO_2 as a result of the reversible condensation - decarboxylation reaction.

Scheme 3. Mechanism of MIPK disproportionation to acetone and DIPK in the presence of CO_2 and water.

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/g-cat/hr	TOF, $\times 10^{-3} \text{ s}^{-1}$	Average TOF, $\times 10^{-3} \text{ s}^{-1}$
1	Isobutyric-1- ^{13}C	40	1 : 23 : 23	ZK	167.7	15	280	78.3%	94.8%	0.141	0.250	0.206
2	Isobutyric-1- ^{13}C	42	1 : 21 : 21	ZK	167.7	16.5	270	52.6%	94.5%	0.091	0.161	
3	Isobutyric-1- ^{13}C	39	1 : 23 : 23	ZR	155.2	17.3	280	55.6%	94.8%	0.092	0.163	0.142
4	Isobutyric-1- ^{13}C	41	1 : 22 : 22	ZR	155.2	16.5	280	37.4%	94.6%	0.068	0.121	
5	Acetic-1- ^{13}C	39	1 : 16 : 15	ZK	144	6	270	59.6%	92.8%	0.449	0.798	0.713
6	Acetic-1- ^{13}C	42	1 : 15 : 15	ZK	144	5	270	36.4%	92.8%	0.354	0.629	
7	Acetic-1- ^{13}C	41	1 : 15 : 15	ZR	124.2	5	270	16.2%	92.8%	0.178	0.316	0.334
8	Acetic-1- ^{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 .

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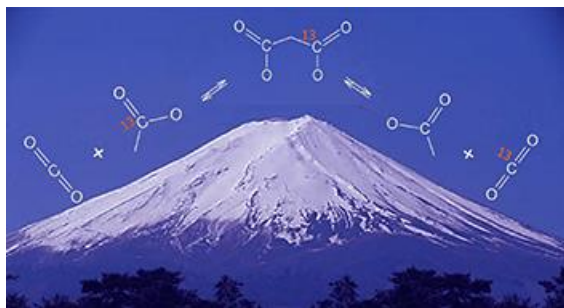
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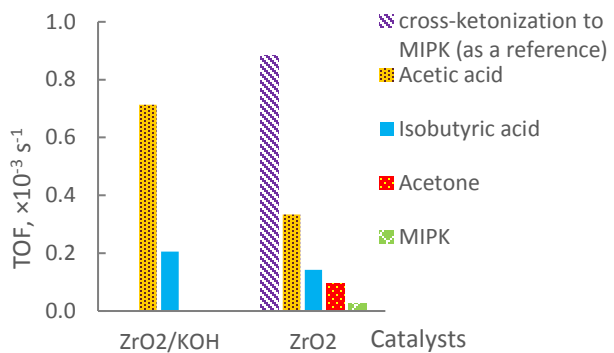


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