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Gas Phase Decarboxylation of Carboxylic Acids

Wilhelm F. Maier, Wolfgang Roth, Irina Thies, and *Paul v. Ragué Schleyer* *

Institut für Organische Chemie der Universität Erlangen-Nürnberg,
Henkestraße 42, D-8520 Erlangen

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Decarboxylierung von Carbonsäuren in der Gasphase

Ein neues einfaches Verfahren zur Decarboxylierung nicht aktivierter Carbonsäuren ist die heterogene Gasphasen-Katalyse unter Normaldruck mit Wasserstoff als Reaktionsmedium. Nickel-Katalysatoren decarboxylieren tertiäre aliphatische, aromatische und araliphatische Carbonsäuren bei 180°C, während Palladium-Katalysatoren bei 330°C zur Decarboxylierung von primären und sekundären aliphatischen sowie aromatischen Carbonsäuren geeigneter sind. Selbst Phthalsäureanhydrid wird mit Palladium-Katalysatoren vollständig defunktionalisiert.

The decarboxylation of carboxylic acids appropriately activated by additional functional groups is one of the standard organic synthetic methods(2). In contrast, the direct decarboxylation of unactivated carboxylic acids requires drastic conditions; yields and selectivities are generally low(3). The problems are associated with the high transition state energies; loss of CO_2 is thermodynamically just as favorable as the decarboxylation of "activated" carboxylic acids, e. g.,(4):

$$\begin{array}{lcc} & \Delta G^\circ & \Delta H^\circ \\ CH_3CO_2H \longrightarrow CH_4 + CO_2 & -68.5 & -33.5\ \text{kJ/mol} \\ C_6H_5CO_2H \longrightarrow C_6H_6 + CO_2 & -54.3 & -20.4\ \text{kJ/mol} \end{array}$$

Despite this exothermicity, indirect methods usually are employed for the removal of unactivated CO_2H groups(5). The *Hunsdiecker* reaction involves the formation of heavy metal salts followed by halogenation and thermal decomposition. The resulting alkyl halide must then be converted to the parent hydrocarbon. The whole reaction sequence, requiring considerable experimental effort, sometimes affords only low yields of hydrocarbon product. A commonly used method, conversion of the carboxylic acid to a *tert*-butyl perester followed by decomposition in the presence of a hydrogen atoms donor, also suffers from experimental difficulties and relatively low yields(6). More recently introduced procedures, e. g., decarboxylation in the presence of lead tetraacetate(7) or thallic acetate(8), often result in the formation of complex reaction mixtures. The same is true for the *Kolbe* electrolysis of carboxylic acids(9). The catalytic reduction of fatty acids to hydrocarbons requires extreme conditions and gives mixtures of products in low yields(10).

Classical examples of the experimental problems associated with decarboxylation are found in the *Prelog* synthesis of adamantane(11) and the syntheses of cubane(6a) and pentaprismane(6b) by *Eaton*. In each case, decarboxylation gives the worst yields of any step. The development of reaction conditions and simple methods for the direct decarboxylation of unactived carboxylic acids is thus a challenge for the synthetic organic chemist. We found earlier that a variety of substituted

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adamantanes can be defunctionalized by gas phase hydrogenolysis on a Ni/Al_2O_3 catalyst. The high yield transformation of 1-adamantanecarboxylic acid into adamantane under these conditions is particularly noteworthy[12].

However, when we examined the more general extension of this gas phase method with Ni catalysts, problems arose. Table 1 summarizes our findings. Good results were obtained with the tertiary acid, 1-adamantanecarboxylic acid (no. 1), benzoic acid (no. 3) and phenylacetic acid (no. 4), which are transformed quantitatively into the parent hydrocarbons. 1-Naphthoic acid (no. 5) is also decarboxylated, but the product is contaminated by the hydrogenated derivatives, tetralin and decalin. The aliphatic acids heptanoic and octanoic acids (no. 6 and 7) gave only moderate to low yields of hydrocarbon. The yields could not be improved further. Even lower yields were obtained with the secondary cyclooctanecarboxylic acid (no. 8), and ε-caprolactone (no. 9) did not react under the conditions employed.

Table 1. Decarboxylation of Carboxylic Acids in the Gas Phase

No.	Compound	Product	Ni catalyst[a) % Yield	Pd catalyst[b) % Yield
1	1-Adamantanecarboxylic acid	Adamantane	95	30
2	1-Methyl-1-cyclohexanecarboxylic acid	Toluene		60
3	Benzoic acid	Benzene	96	95
4	Phenylacetic acid	Toluene	95	97
5	1-Naphthoic acid	Naphthalene	33	–
6	Heptanoic acid	Hexane	26	98
7	Octanoic acid	Heptane	64	97
8	Cyclooctanecarboxylic acid	Cyclooctane	20	85
9	ε-Caprolactone	Pentane	0	85
10	3,3-Dimethylbutyric acid	Neopentane	–	96
11	*endo*-2-Norbornanecarboxylic acid	Norbornane	9	96
12	*endo*-2-Norbornaneacetic acid	2-Methylnorbornane[c)		96
13	Cyclopentanecarboxylic acid	Cyclopentane + Cyclopentene		40 45
14	Salicylic acid	Benzene		97
15	Levulinic acid	2-Butanone		0
16	Phthalic anhydride	Benzene		97

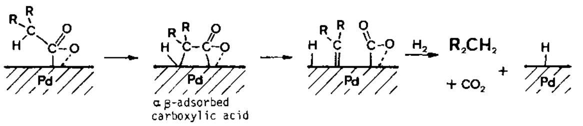
[a) Conditions: catalyst temperature 180 °C, H_2 flow 25 ml/min. – [b) Conditions: catalyst temperature 330 °C, H_2 flow 25 ml/min. – [c) *Exo-endo* ratio 1 : 1.2.

Since attempts to improve the yield of decarboxylation product from aliphatic acids failed, effective gas phase decarboxylation with the Ni catalyst appears to be restricted to tertiary aliphatic, to aromatic, and to araliphatic carboxylic acids. Besides the tendency to hydrogenate the aromatic rings at temperatures below about 250 °C, Ni catalysis also may result in unactivated C–C bond cleavage at temperatures between 150 °C and 280 °C[13]. This reaction decreases the selectivity of the process at higher temperatures. The intolerance of the Ni catalyst towards all other functional groups[12] is another drawback. Lower temperatures are best to avoid side reactions, but most carboxylic acids of interest will either not be volatile at 180 °C or will contain additional functional groups.

During investigations of simple catalytic routes for the preparation of dodecahedranes, we discovered that palladium catalyses decarboxylation more effectively than nickel[14]. In particular, the unactivated aliphatic acids, heptanoic and octanoic acids (no. 6 and 7), were decarboxylated quantitatively in the presence of Pd/SiO_2 and H_2 at 330 °C. Table 1 summarizes the experimental results. In contrast to the Ni catalysis, heptanoic and octanoic acids (no. 6 and 7) as well as cyclooctanecarboxylic acid (no. 8) and ε-caprolactone (no. 9) underwent clean decarboxylation by Pd-catalysis. Benzoic acid (no. 3) and phenylacetic acid (no. 4) are transformed to the aromatic hydrocarbons without hydrogenated by-products. Even the sterically hindered 3,3-dimethylbutyric acid (no. 10) is converted to neopentane smoothly.

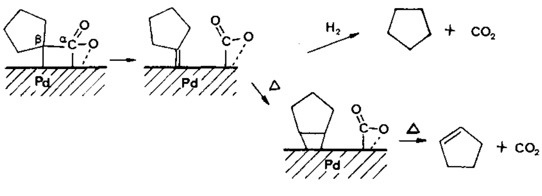
The facile decarboxylation of the strained norbornanecarboxylic (no. 11) and norbornaneacetic (no. 12) acids demonstrate that palladium, in contrast to nickel[13,15], does not disrupt the carbon skeleton under the conditions employed.

An exception, curiously, was 1-adamantanecarboxylic acid (no. 1) – the only aliphatic acid decarboxylated in good yield with the nickel catalyst. However, the low yield obtained reproducably with the Pd catalyst is mainly due to the failure of the acid to pass through the catalyst bed. Recovery attempts, heating to 430 °C in the presence of H_2, destroyed the adsorbed material and reactivated the catalyst. Similar problems were found with 1-methyl-1-cyclohexanecarboxylic acid (no. 2) which required long reaction times and gave only moderate yields (toluene was obtained under these conditions). Tertiary carboxylic acids may therefore decompose by a different mechanism than other acids. Primary and secondary acids contain hydrogen atoms α to the carboxyl group, but tertiary acids do not and cannot undergo α-coordination. α,β-Adsorption (Scheme 1), also possible for aromatic acids, is believed to be the key mechanistic step during C – C hydrogenolyses[13,16] as well as during H/D exchange in heterogeneous gas phase reactions[17].



Scheme 1. Speculative interpretation of the decarboxylation mechanism

Another surprise was the detection of major amounts of cyclopentene formation during decarboxylation of cyclopentanecarboxylic acid (no. 13). While palladium is an effective hydrogenation catalyst, cyclopentene, once formed, probably passes through the catalyst zone at 330 °C too rapidly for hydrogenation to be complete. This olefin formation suggests catalyst attack at the α-position to the carboxyl group, and supports the proposed mechanism. Scheme 2 shows a schematic representation of olefin formation, but this is speculative and other mechanisms are not excluded. At higher temperatures, palladium can function as a dehydrogenation catalyst, but the thermodynamics are unfavorable at 330 °C.



Scheme 2. Mechanistic interpretation of the decarboxylation of cyclopentanecarboxylic acid (no. 13)

The overall reaction can be written as:

$$RCO_2H \longrightarrow RH + CO_2$$

However, this formulation, while supported by the formation of CO_2 product, suggests that the hydrogen used as reaction gas may not be necessary. The contrary is true. The complete recovery of unchanged heptanoic acid when N_2 instead of H_2 was used as carrier gas underscores the importance of hydrogen. Since no hydrogen is needed in the overall stoichiometry, the active catalytic site may not be Pd itself but rather a Pd/H complex. After loss of CO_2, the R group, adsorped on the catalyst surface (perhaps at more than one site) reacts with hydrogen. Our attempts to learn more about the mechanism of this reaction by using deuterium in place of hydrogen as the carrier gas were frustrated by the massive H/D exchange observed. Such H/D exchange occurs faster than decarboxylation under these conditions. Palladium is generally activated by hydrogen (even for dehydrogenation reactions in which hydrogen is produced). Perhaps the desorption of organic substrates from active catalytic sites is promoted by hydrogen[18].

The remarkable activity of palladium as decarboxylation catalyst prompted us to investigate the behaviour of these catalytic conditions towards other functional groups. Defunctionalization of salicylic acid (no. 14) resulted in quantitative benzene formation; the phenolic hydroxyl group was also removed. In contrast, *n*-hexanol was recovered (50%) under identical conditions. Ketones like norbornanone and 3-hexanone passed over the catalyst unchanged almost quantitatively, but levulinic acid (no. 15), a γ-ketocarboxylic acid, suffered complete decomposition under the same conditions.

Anhydrides, an easily accessable and unusually stable class of organic molecules, will be the subject of further investigations. Indeed, the first compound studied, phthalic anhydride (no. 16), was smoothly transformed to benzene by Pd catalysis.

Conclusions

A variety of carboxylic acids can be decarboxylated smoothly in the gas phase with Ni and Pd catalysts. The use of hydrogen as reaction gas is essential. This suggests that other decarboxylation methods may also benefit from the presence of hydrogen and we intend to explore this possibility.

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Experimental Part

Mass spectra: Varian CH 4B MAT, 70 eV. – GC-MS analyses: Finnigan 3200 E instrument (25 m capilliary column, SE 30, 70 eV). Gas chromatographic analysis: Perkin Elmer Sigma 1 (11 m SE 30 and 25 m Carbowax capilliary columns). Perkin Elmer 990 (1 m Porapack QS).

Materials: All carboxylic acids as well as the hydrocarbon products are commercially available. All reaction products were identified by direct comparison with authentic materials.

Catalyst: The preparation of the Ni/Al_2O_3 catalyst has been described elsewhere[13].

Pd Catalyst: to 150 mg $Pd(NO_3)_2$, dissolved in 20 ml water, 1.0 g of support (Kieselgel Woelm DC) was added. The water was evaporated on a rotary evaporator and the residue dried for 4 h at 120 °C in an oven. The material was ground and packed between glass wool plugs in a Pyrex tube (diameter 6 mm) and reduced by means of hydrogen (flow rate 20 – 30 ml/min). The temperature was increased slowly: 130°C, 40 min; 180°C, 100 min; 210°C, 40 min; 250°C, 80 min; 280°C, 40 min; 330°C, 30 min; 380°C, 30 min; 430°C, 60 min. The resulting Pd/SiO_2 catalyst could be used (after reactivation at 400°C for 30 min) for *several* experiments without significant loss of activity.

Experimental Procedure: The decarboxylation of the various carboxylic acids was carried out in a flow apparatus[13]. The general decarboxylation procedure is described for *heptanoic acid* (no. 6):

Heptanoic acid (no. 6) (834 mg, 6.41 mmol) was placed in a U-tube and heated in an oil bath slowly up to the boiling point (219°C) in temperature steps of 20°C/15 min. A slow stream of hydrogen (25 ml/min) was used to pass the acid through a catalyst-containing Pyrex tube, which was heated to 330°C. The furnace was controlled by a Fischer Proportionalregler 0120. The product was collected in a U-tube, cooled by liquid nitrogen. Since H_2O and CO_2 are produced, ice and dry ice are also collected. The separated hydrocarbon product (540 mg = 98% yield), identified by NMR and glc by comparison with an authentic sample, was pure *n-hexane*.

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