



# Oxidative ring-opening of aromatics: Thermochemistry of iron, copper and cobalt biphenyl carboxylates

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## ABSTRACT

Thermochemistry of aromatic carboxylates has received little attention in the literature, despite their relevance as intermediates in the oxidative ring-opening of aromatic compounds. The thermal behavior of selected transition metal aromatic carboxylates was studied as a first step to determine the effectiveness of the metals as potential catalysts for decarboxylation. Iron, cobalt, and copper salts of biphenyl carboxylic acids were synthesized and their thermal behavior over the temperature range 25–600 °C was investigated. Characterization of these compounds indicated that, with exception of the copper (II) biphenyl-2-carboxylate, all metal carboxylates corresponded to homogeneous materials of different morphology. Structures in which metals might be present in more than one oxidation state or forming metal–metal bonds are possible. Infrared spectroscopy showed that all synthesized carboxylates existed in bridging configuration. In all cases, thermal analysis revealed a complicated behavior. Decomposition occurred as a multistage process and exhibited a rather complex mechanism. The decomposition of the iron and copper carboxylates resembled a cascade of reactions, i.e., the individual decomposition steps could not be resolved due to overlapping; whereas, the decomposition of the cobalt compounds followed a more stepwise type of process, i.e., the individual decomposition steps could be differentiated. Aromatic carboxylates of moderate thermal stability, with decomposition temperatures above 240 °C, were formed. Thermal stability depended on the metal and increased in the order  $\text{Cu} < \text{Fe} < \text{Co}$ . Production of benzoic acid during the decomposition of the copper carboxylates was observed. Production of fluorenone suggested that the Fe, Co and Cu carboxylates decomposed, at least partially, via the formation of an organic ketone and metal oxides. In the case of the copper carboxylates, the reduction of the copper by forming cuprous oxide ( $\text{Cu}_2\text{O}$ ) also took place.

## 1. Introduction

Oxidative ring-opening has been explored as an alternative approach for the upgrading of heavy aromatic materials such as heavy oils, bitumens, asphalts, and coal liquids [1,2]. The overall oxidative ring-opening process involves three reaction steps: (1) oxidation of multinuclear aromatics to produce quinonoids, (2) further oxidation to form ring-opened carboxylic acids, and (3) decarboxylation to remove carboxylic acids as  $\text{CO}_2$ . During the latter step, decarboxylation competes with side-reactions, such as ketonization and dehydration, which decreases the selectivity of the reaction towards ring-opened products [2]. The use of a catalyst to favor decarboxylation is necessary.

It has been demonstrated that metal carboxylates can be used as surrogates for the reaction of carboxylic acids over heterogeneous catalysts when investigating their catalytic decomposition [3]. This characteristic found particular application in the study of the decomposition of biphenyl carboxylic acids, which are products of the

oxidative ring-opening of phenanthrene. Specifically, decomposition of zinc biphenyl carboxylates indicated that when zinc facilitated the reaction, the selectivity towards the ring-opened product, *biphenyl*, always exceeded the selectivity towards the ring-closed product, *fluorenone* [2]. In other words, catalytic decomposition, as opposed to thermal decomposition, increased the selectivity to ring-opened products by favoring decarboxylation (Fig. 1).

The study of zinc biphenyl carboxylates [2] highlighted the potential selectivity benefit of catalytic carboxylic acid decomposition over thermal decomposition. It also suggested that the temperature and chemistry of aromatic carboxylic acid decomposition may change depending on the metal used during the reaction. Unfortunately, there was little data in the literature about the thermal behavior and thermal stability of aromatic carboxylates that could help to predict which materials would be good candidates for carboxylic acid decomposition.

The use of alkali and alkaline earth metals for carboxylic acid decomposition was explored [4]. Thus, the thermochemistry of biphenyl-

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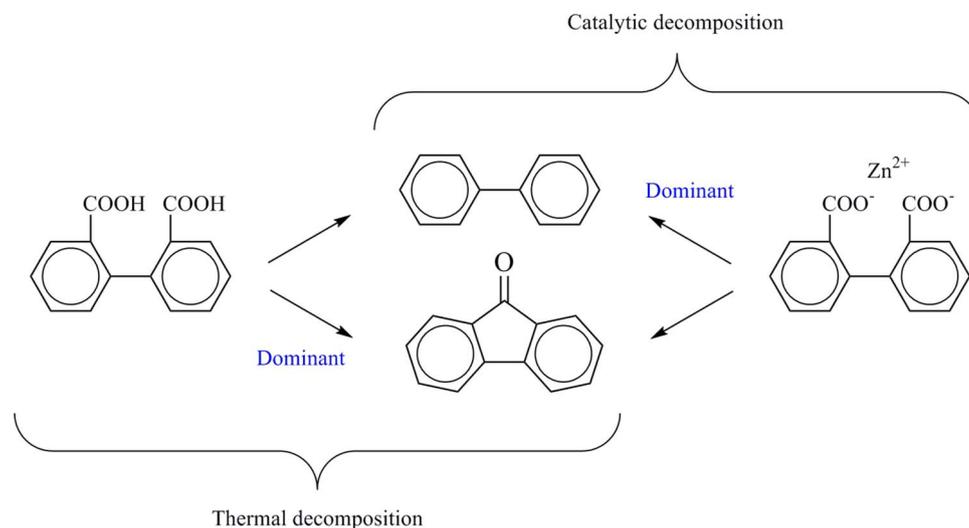


Fig. 1. Dominant thermal decomposition pathways of biphenyl-2,2'-dicarboxylic acid and zinc biphenyl-2,2'-dicarboxylate at around 380 °C.

2,2'-dicarboxylates of sodium, potassium, and magnesium was investigated [4]. It was found that the strong basic properties of alkali and alkaline earth metals resulted in the formation of thermally stable carboxylates with decomposition temperatures above 400 °C. Although catalytic decomposition at such high temperatures does not preclude consideration of these materials as catalysts, it is likely that catalytic and thermal decomposition would occur in parallel, with an associated loss in selectivity to ring-opened products (e.g. biphenyl). As a result, metal carboxylates with lower decomposition temperatures to limit the contribution of thermal decomposition during catalytic decomposition were sought.

Unfortunately, there is again little information in literature on the thermochemistry of transition metal carboxylates, even for the alkanoates [5]. A couple of relevant studies are found in *this journal* [6–11]. Transition metals generally form carboxylates with lower decomposition temperatures than the corresponding carboxylates of alkali and alkaline earth metals. Thus, transition metals could be more promising candidates as decomposition catalysts.

In this study, the thermochemistry of selected transition metals biphenyl carboxylates is investigated. Iron, cobalt, and copper biphenyl-2,2'-dicarboxylates, as well as cobalt and copper biphenyl-2-carboxylates were synthesized and their thermal behavior studied. Determining the thermochemistry of iron, copper and cobalt biphenyl carboxylates is the first step towards elucidating their decomposition reaction network by reactor studies.

## 2. Experimental

### 2.1. Materials

Iron, cobalt, and copper salts of biphenyl carboxylic acids were synthesized from commercially available materials. Chemicals, calibration materials and gases used for the synthesis and the thermal analysis are listed in (Table 1).

### 2.2. Synthesis of the metal carboxylates

Metal carboxylates were prepared by neutralization according to the general synthesis procedure for reaction in non-aqueous media described by Mehrotra and Bohra [12]. The corresponding metallic element or an appropriate metal-containing compound, such as hydroxide or carbonate, was mixed with a slight excess (2% molar excess) of the carboxylic acid. In this study, biphenyl-2-carboxylic acid and biphenyl-2,2'-dicarboxylic were used.

Synthesis of the iron carboxylate employed direct reaction of metallic iron and the corresponding carboxylic acid. Tetrahydrofuran was used as solvent. Synthesis of the cobalt and copper salts used ethanol as solvent, and the corresponding hydroxides as the metal-containing material. In the case of the copper biphenyl-2-carboxylate, the synthesis was carried out using both copper hydroxide and copper (II) carbonate basic. The estimated purity of the metal carboxylate obtained using the latter compound was higher, and so, it was used to perform all subsequent experimental work. In all cases, the reaction mixture was heated at 60 °C, under total reflux, and stirred for several hours until completion of the reaction. Metal carboxylates were recovered by evaporation of the solvent at reduced pressure conditions (80 kPa, absolute), using a rotary evaporator (Heidolph, Model Hei-VAP Precision with Glassware Set G3). The iron biphenyl-2-carboxylate could not be obtained under the experimental conditions employed; therefore, it is not part of the present study.

After recovery, all synthesized metal carboxylates were thoroughly washed with acetone, and then dried at approximately 100 °C until they reached constant mass. The final solid products were finely ground and stored in a desiccator.

### 2.3. Equipment and procedure

#### 2.3.1. Characterization of metal carboxylates

Synthesized biphenyl transition metal carboxylates were characterized. Infrared (IR) spectroscopy was used to confirm that the carboxylic acid used in the synthesis was converted into the carboxylate. Scanning electron microscopy with microanalysis by energy dispersive X-ray spectroscopy (SEM-EDS) was used to assess homogeneity and check for inorganic impurities. Elemental analysis and inductively coupled plasma optical emission spectrometry (ICP-OES) were employed to determine the metal content.

Infrared spectroscopy was employed to confirm the synthesis of the metal carboxylates. It was performed with an ABB MB3000 Fourier transform infrared spectrometer equipped with a Pike MIRacle Reflection attenuated total reflectance (ATR) diamond crystal plate and pressure clamp. The spectra were collected with Horizon MB™ FTIR Software, at a resolution of 4 cm<sup>-1</sup>, using an average of 120 scans over the spectral region 4000–500 cm<sup>-1</sup>.

Infrared spectroscopy was also used to estimate the amount of unreacted carboxylic acid that remained as an impurity in the metal carboxylates. Selected samples of the metal carboxylates were spiked with a known amount of the corresponding parent carboxylic acid. The IR spectra of these samples were collected and further processed to

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