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Oxidative ring-opening of aromatics: Thermochemistry of sodium, potassium and magnesium biphenyl carboxylates

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ABSTRACT

Oxidative ring-opening is a potential alternative to hydrodearomatization and cracking for the conversion of multinuclear aromatic compounds to lighter products. Oxidation of multinuclear aromatics produces quinonoids that can be ring-opened by forming carboxylic acids, which can be decarboxylated to produce lighter oxygen-free hydrocarbons. The efficiency of this reaction depends on the thermochemistry of the metal carboxylate intermediate. Undesirable side-reactions compete with decarboxylation. Using metal carboxylates as catalytic surrogates is a convenient strategy to investigate the catalytic decomposition of carboxylic acids. The thermal behavior of sodium, potassium and magnesium biphenyl-2,2′-dicarboxylates was investigated, over the temperature range 25 to 600 °C, to evaluate the suitability of these metals as catalytic materials for decarboxylation, as well as to gain an understanding of the steps involved in the decomposition. In all cases, thermal analysis revealed quite complex behavior. Thermal events including the loss of lattice water, phase transitions and decomposition were observed. The strong basic properties of alkali and alkaline earth metals resulted in the formation of thermally stable carboxylates with decomposition temperatures above 400 °C. Infrared spectroscopy indicated that the Na, K and Mg carboxylates all existed in ionic (or bridging) configuration, but a bidentate type of interaction was additionally observed for the magnesium carboxylate. Formic acid was also identified during the initial stages of sodium biphenyl-2,2′-dicarboxylate decomposition suggesting the formation of an ester intermediate (not confirmed). The thermal stability of the biphenyl-2,2′-dicarboxylates increased in the order Na < K < Mg, which differed from thermal stability sequence of the alkanoates.

1. Introduction

Multinuclear aromatic compounds are common in the high-boiling distillation fractions of oils and coal liquids. Conventional refining technologies used for the conversion of these materials include visbreaking, coking, catalytic cracking, and residue hydroconversion [1]. Oxidative ring-opening is a potential alternative reaction pathway for the conversion of multinuclear aromatics to lighter and less refractory products. The aim of this conversion chemistry is to partially oxidize multinuclear aromatic compounds to its quinonoid form, and then, with further oxidation to convert the quinonoid to a carboxylic acid, leading to the opening of the aromatic ring [2,3]. In the last step, decarboxylation of the aromatic carboxylic acid, eliminating the added oxygen as CO_2, takes place.

Unfortunately, undesirable side-reactions, such as ketonization and dehydration, compete with decarboxylation, decreasing the selectivity of the reaction towards the ring-opened products. Using a catalyst to facilitate the decarboxylation step is therefore necessary [3].

Catalysis of carboxylic acid decomposition proceeds via metal carboxylate intermediates and the activity and selectivity of decomposition depend on the metal. Interestingly, the reaction on a heterogeneous catalyst can be approximated by decomposition of the metal carboxylate in isolation. The catalytic activity of a metal or metal oxide for carboxylic acid decomposition relates to the thermal stability of the corresponding bulk metal carboxylate [4]. Thermal analysis is therefore a useful and powerful tool to study the catalytic decomposition of carboxylic acids.

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Biphenyl-2,2′-carboxylic acid is the product from oxidative ring-opening of phenanthrene, which is used as model compound to represent multinuclear aromatics. In this work, selected alkali and alkaline earth metals are investigated as potential decarboxylation catalysts for biphenyl-2,2′-carboxylic acid. It is known that Na and K supported on Al_2O_3, as well as MgO as a bulk metal oxide, are all basic catalysts [5,6]. Basic catalysis would readily form surface carboxylates that could lead to decarboxylation. Furthermore, these are not scarce or expensive materials and can readily be manufactured as bulk heterogeneous catalysts. Alkali metal and alkaline earth metal catalysts are therefore attractive from both an economic and an application point of view.

The aim of this work was to investigate the thermochemistry of selected alkali and alkaline earth metal biphenyl carboxylates to determine the potential suitability of sodium, potassium and magnesium as materials for decarboxylation catalysts. Unfortunately, there appeared to be no data on the thermal behavior or the thermal stability of these organic salts, such data was available only for some of the metal alkanoates [7].

A secondary objective was to compare the thermochemistry of these metal carboxylates, where the carboxylate group is attached to an aromatic, to the thermochemistry of alkanoates, were the group is attached to an aliphatic chain. Any generalizations would be helpful in future work, since it would enable inferences to be drawn from data for the metal alkanoates, which is more readily available.

2. Experimental

2.1. Materials

Sodium, potassium and magnesium biphenyl-2,2′-carboxylates, the compounds of study, were not commercially available and had to be synthesized. These metal carboxylates were prepared from commercially obtained materials. The chemicals, calibration materials and cylinder gases used are listed in Table 1.

2.2. Synthesis of the metal carboxylates

Metal carboxylates were synthesized by mixing an appropriate metal-containing compound, such as a metal hydroxide or metal carbonate, with a slight excess (2% molar excess) of the biphenyl-2,2′-dicarboxylic acid. The solvent and temperature selected for the synthesis varied depending on the metal used for reaction as is indicated.

Sodium biphenyl-2,2′-dicarboxylate and potassium biphenyl-2,2′-dicarboxylate were prepared according to the work of Franzosini, et al. [8,9]. Biphenyl-2,2′-dicarboxylic acid was mixed either with sodium or potassium carbonate, using methanol as a solvent. The reaction mixture was stirred for several hours without heating. The metal carboxylates were recovered by evaporation of the solvent under reduced absolute pressure (80 kPa, absolute), using a rotary evaporator (Heidolph, Model Hei-VAP Precision with Glassware Set G3). Purification of the alkali metal carboxylates was conducted by recrystallization. A mixture of ethanol and methanol (1:1 by volume) was used to obtain the sodium carboxylate, whereas a mixture of 2-propanol, ethanol and methanol (4:2:1 by volume) was employed in the case of the potassium carboxylate.

Magnesium biphenyl-2,2′-dicarboxylate was synthesized based on the general synthesis procedure for reactions in non-aqueous media described by Mehrotra and Bohra [10]. Ethanol was used as solvent and magnesium hydroxide as the starting metal-containing material. The reaction mixture was heated to and kept at 60 °C (total reflux) and stirred for several hours until completion of the reaction. Once the metallic salt precipitated, it was recovered by evaporation of the solvent at reduced pressure conditions as outlined before.

After recovery and purification, 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 were stored in a desiccator. The purity of the synthesized metal carboxylates was evaluated and it is reported in Table 2.

2.3. Equipment and procedure

Fourier transform infrared (FTIR) spectroscopy and ^{1}H Nuclear Magnetic Resonance (NMR) were used to confirm the chemical identity of the synthesized metal carboxylates. The former was also used in the analysis of the products obtained after thermal analysis. Infrared spectra were collected using an ABB MB3000 Fourier Transform Infrared spectrometer with Horizon MB^{TM} FTIR software. The spectrometer was equipped with a Pike MIRacle Reflection attenuated total reflectance (ATR) diamond crystal plate. Spectra were collected at a resolution of 4 cm^{-1}, using an average of 120 scans over the spectral region of 4000–500 cm^{-1}. On the other hand, ^{1}H Nuclear Magnetic Resonance (NMR) spectra were obtained in a Nanalysis 60 MHz NMReady – 60 spectrometer with Mnova NMR software. The equipment was pre-calibrated with deuterated dimethyl sulfoxide (DMSO-d_6). Close to 8.5 mg of sample were dissolved in 0.7 mL of deuterated dimethyl sulfoxide, placed in NMR tubes and analyzed using the following parameters: spectral width 14 ppm; scans per sample: 128; average scan time: 25.5 s.

The thermal behavior of the synthesized compounds was studied through differential scanning calorimetry (DSC). A normal pressure differential scanning calorimeter (Mettler–Toledo DSC 1) was used. This equipment is a heat flux (disk) type calorimeter and is equipped with FRS-5 sensor. The sample chamber nitrogen flow rate and the sheathing nitrogen flow rate were kept at 100 mL min^{-1} during all of the experiments. Standard 40 μL aluminum (Al) crucibles with perforated lids were employed for all thermal analyses. Samples were weighed on an analytical balance (Mettler–Toledo, Model XS105 Dual Range Analytical Balance) with 10 μg readability in the range of 0–105 g. The typical sample sizes employed for DSC varied between 6 and 10 mg. All metal carboxylates were analyzed in the 25 to 550 °C temperature range at a heating rate of 10 °C min^{-1}. The experimental work was conducted in nitrogen atmosphere and analyses were performed in triplicate. Reversibility of the thermal events was confirmed by heating the sample just past the observed transition, and then the cooling down below the event and heating up again. All heating segments employed a heating rate of 10 °C min^{-1} and all cooling segments employed a cooling rate of −10 °C min^{-1}. The temperature and heat flow calibration of the DSC was regularly checked by determining the onset of melting and enthalpy of melting of indium. The temperature measurements were accurate to within 0.4 °C and the enthalpy measurements were accurate to within 3.5% relative over multiple calibration checks expressed as sample standard deviations from literature values for indium (156.6 °C and 28.6 J g^{-1} [11]).

Visual observation of the thermal events was carried out using an Olympus BX51 microscope and Mettler FP84HT TA Microscopy Cell (DTA/DSC sensor) with FP90 central processor. Samples were placed in transparent glass crucibles of 7 mm in diameter. Glass cover disks of also 7 mm in diameter were used as lids. Samples were subjected to a temperature program in the range 25 to 375 °C.

Decomposition and mass loss profiles of the metal carboxylates were investigated by thermogravimetric analysis (TGA). A Mettler Toledo TGA/DSC1 system, equipped with a LF 1100 furnace, a sample robot and a MX5 internal microbalance (5 g range and 1 μg readability) was used to collect the experimental data. Sam-