

Synthesis and Characterization of Benzilate Esters as Aqueous Corrosion Inhibitors for Mild Steel and 2024, 6061, and 7075 Aluminum Alloys

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Abstract

In this investigation, synthesis and characterization of environmentally friendly metallo-organic corrosion inhibitors for protection of mild steel and certain aluminum alloys are being sought to replace hexavalent chromium based corrosion inhibitors. For this reason, several corrosion inhibiting species such as benzoic acid and metal oxyanions were combined in a single compound with the general formula, $(M)_x(\text{benzoic acid})_y(M'_aO_b)_z$. First group of such compounds were synthesized in a similar study of the first author reported in another study with the title of "Synthesis and Characterization of Salts and Esters of Hydroxy Acids as Corrosion Inhibitors for Mild Steel and Aluminum Alloys" and this work aims to build on the success of those compounds since theoretically, there is no reason why benzoates cannot be good replacements for α -hydroxy acids such as gluconates. Additionally, benzoates are less soluble in general than hydroxy acids, which could result in a corrosion inhibiting compound with an optimum window of solubility. Practical results have mostly proven the hypothesized advantages of benzoates correct and yielded that certain salts and esters of benzoates can be suitable corrosion inhibitors for certain metals and their alloys.

Keywords: characterization, synergistic, carcinogenic, precursor

1. Introduction

In this study, compounds that possess the general formula of $(M)_x(\text{benzoic acid})_y(M'_aO_b)_z$ are synthesized and characterized. As the components of these formulations, constituents that are already proven as corrosion inhibitors are tried. Among them are zinc and calcium cations making up the cationic constituent (M); especially zinc cations are very well-known for their cationic inhibiting efficiencies. Metal oxyanion constituent, which leads to an ester derivative of the benzoates are also chosen amongst constituents that are already proven as corrosion inhibitors especially for iron and steel alloys such as molybdates, borates and vanadates. Benzoic acid is the constituent here, which the study aims to produce synergistic formulations of and these synergistic formulations are hoped to possess the combined individual corrosion preventive characteristics of its constituents. Benzoate salts and esters will be further tested alongside the individual components in order to determine whether there are any synergistic interactions. It is important to note that most of the chosen individual components are corrosion inhibitors that were previously commercialized as well.

2. Materials and Methods

All reagents were ACS reagent grade or higher and used without further purification. Small amounts of reactants, such as 20 mmol equaling to one equivalence, were refluxed in 100 ml up to several hundred ml of distilled water for a few hours up to a period of overnight, followed by the isolation of product mostly via rotary evaporation or by precipitation in methanol given the product is not soluble in methanol. Please refer to Table 1 for further details.

Table 1. Designated Reagent/Solvent Amounts for Synthesis Reactions

Product	Reagents	Amount (mmols)	Water/Soln. (ml)	Additional Information
Potassium Benzilate	Potassium Carbonate	10	200	Room Temp.
	Benzilic Acid	20		
Potassium Benzilate	Potassium Benzilate	20	200	reflux
Molybdate	Molybdenum Trioxide	10		
Potassium Benzilate Vanadate	Potassium Benzilate	20	200	reflux
	Vanadium Pentaoxide	10		
Potassium Benzilate Borate	Potassium Benzilate	20	200	
	Boric Acid	20		
Zinc Benzilate Molybdate	Zinc Chloride	20	100	room temp.
	Potassium Benzilate	20		
	Molybdate			
	2N Ammonium Hydroxide	200		

Additional Information:

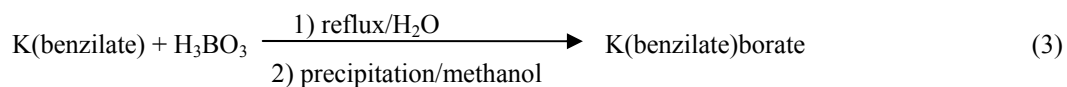
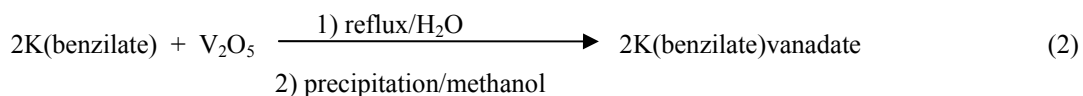
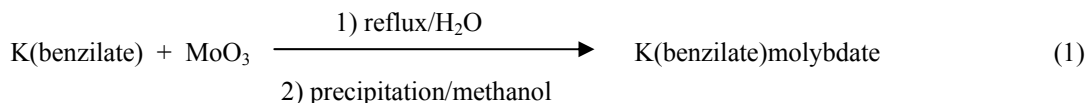
In addition to the mentioned amounts of reagents, very high amounts of reagents were also used in the same proportions to synthesize products in bulk amounts when needed in weight-loss and salt fog chamber tests.

Yield was not measured for many products due to their very high hygroscopic nature leading to errors.

2.1 Syntheses of Benzilate Salts and Their Metal Oxyanion Esters

For the syntheses of metal oxyanion benzilates, first potassium benzilate was synthesized by dissolving 20 mmols of benzilic acid in about 200 ml distilled water. Later 10 mmols of K_2CO_3 was added to the stirred benzilic acid solution at a rate that avoided foaming of the solution by the released carbon dioxide.

Next the potassium benzilate solution obtained from the first step was refluxed with the corresponding metal oxide in water until a clear solution was obtained. The products were relatively easier to isolate than the corresponding gluconate esters due to their less hygroscopic nature. An exception was dark gray-black K(benzilate)vanadate that was kept in solution due to its highly hygroscopic nature compared to other benzilate esters. After several months the initially soluble K(benzilate)vanadate particles were observed to precipitate out of the solution forming a brown precipitate compared to the initial dark grayish color. Filtering this solution and attempting to redissolve it in water easily led to the formation of a suspension that is stable for several days.



2.2 Solubility Measurements

An inhibitor concentration of 200 ppm or less for a system of 100 ml of distilled water solution has been determined as an optimum concentration. The concentration unit has been chosen as ppm (part per million) for reasons of convenience considering performing several thousands of tests with using very small amounts of inhibitors. In most cases however, molecular weights of the tested inhibitors were 200 g/mol and higher due to high weights of hydroxy-acid constituents such as gluconates and benzilates, which corresponds to a concentration range of 0.01 M for a molecular weight of 200 g/mol and 0.005 M for a molecular weight of 400 g/mol, thus leading to comparable inhibition efficiency values with little error caused by concentration discrepancies. These seemingly low concentrations were often sufficient since the corrosion process itself is not a very fast process. Thus, the supply provided by a low-solubility inhibitor was sufficient unless the environment is too warm or contains very high concentrations of aggressive anions especially in the case of mild steel, which is prone to heavy corrosion. In addition to direct inhibition of corrosion, formation of conversion coatings is another desired outcome for longer term corrosion protection. This often requires precipitation of inhibitor products on the metal surface. Thus, optimum solubility is essential for the formation of protective conversion coatings on substrate surfaces.

2.3 Particle Size Measurements

Particle size measurements as shown in Figure 1 have been conducted using a dynamic light scattering particle size analyzer. Other than complimenting colorimeter and flame atomic absorption spectrometer for solubility measurements, average particle size information is also important in engineering of the sol-gel coatings which are designed to incorporate such inhibitors. Particle sizes of very soluble inhibitors were found to be very small. Size distribution by volume graph indicated the Z-average size values to be between 0 and 2 nanometers for the highly water soluble compounds shown below. Some synthesized compounds here such as potassium benzilate vanadate could not be tested due to being amorphous having very large particle sizes.

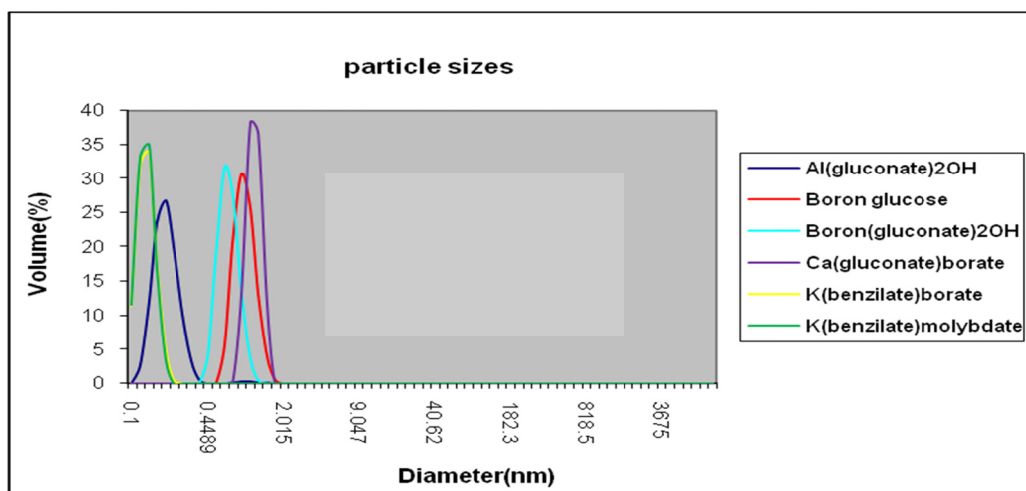


Figure 1. Dynamic light scattering of selected tested compounds

2.4 Surface Area Measurements

The surface area measurements were conducted using a Quantachrom Nova 1200 surface area analyzer, via a nitrogen adsorption isotherm, using the Brunauer-Emmett-Teller (BET) method, and six points in the range of 0.05 to 0.30 P/P₀. A high surface area for an inhibitor is a positive contribution to its inhibition efficiency that correlates with higher reactivity, and more rapid dissolution kinetics. High surface areas may rightfully imply effective barrier properties. As a result surface area measurements, benzilates did not reveal significant specific surface areas with all resulting in values close to 0.

2.5 Powder X-Ray Diffraction Studies

X-ray powder diffraction patterns were recorded on a Bruker AXS D-8 Advance X-ray powder diffractometer

using copper K_{α} radiation. X-ray diffractometer studies did not reveal positive results since the tested compounds were amorphous.

3. Results and Discussion

Compounds, which were tested for their corrosion inhibition properties, were synthesized via a single-source precursor method, which is a relatively easier synthesis method. The problems arose particularly due to the nature of the products, which were too hygroscopic preventing them to be handled for characterization. Such products were kept in solution form even after isolating them. Overall, the syntheses reactions were reproducible regardless of the amounts of the reagents reacted. Characterization studies on the other hand were proven to be difficult first due to amorphous structure of the products, which in turn resulted in no structural information through X-ray analysis. Secondly, difficulty in handling most of these products resulted in very little gravimetric measurements to be performed. Such examples were benzilate esters, which were hygroscopic.

A new group of novel metallo-organic compounds were synthesized and tested for use as chromate replacements in corrosion inhibition applications of mild steel and aluminum alloys. For this reason, certain anions and cations that are well-known for their corrosion inhibiting properties were combined under one formulation with the general formula of $(M)_x(\text{benzilic acid})_y(M'_aO_b)_z$. M denotes the metallic cationic constituent; among them zinc and calcium cations are well established cathodic inhibitors. The second component is the anion of benzilic acid. Benzilic acid yielded synergistic results particularly with metal oxyanions such as vanadates. Both trivalent chromium and zinc carboxylates revealed almost perfect corrosion inhibition efficiency results for aluminum alloys. The third component of the formulation, that is metal oxyanions, were selected among well-established corrosion inhibitors such as molybdates, vanadates, and borates. Molybdates, for instance, are very common corrosion inhibitors for mild steel. These metal oxyanions usually inhibit corrosion by forming lower oxidation state oxides and hydroxides repairing the passive oxide film on the metal substrates. It is reported in the literature that molybdenum(VI)-benzilic acid system forms stable complexes (Cervilla et al., 1995; Cui et al., 2006). One of these complexes is in dimeric structure similar to the structure of gluconate molybdate complex as shown in Figure 2, while the other complex consists of two benzilate ligands along with two molybdenum cores connected via oxygen bridges with formation constants of $\beta = 17.35$ for the former and $\beta = 29.07$ for the latter (Cervilla et al., 1995).

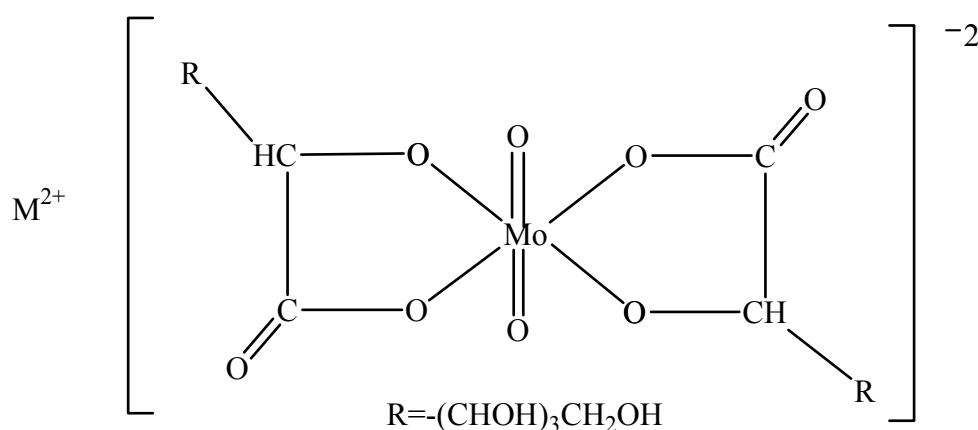


Figure 2. Structure of zinc or calcium gluconate molybdate

Complexes of vanadium(V)-benzilic acid are also mentioned in the literature, however these complexes usually seem to involve another ligand as well such as pyridine, thiol, or salen (Kiparisov et al., 1973; Money et al., 1985; Vergopoulos, 1995; Charykov, 1991; Fan et al., 1988; Du & Xiu, 1984; Belford et al., 1969).

Depending on different types of applications, the range of solubility had a major impact on the efficiency of the corrosion inhibitors. Both in aqueous solutions and in sol-gel coatings, inhibitors must possess an optimum solubility sufficient to migrate to the sites of corrosion and react with corrosive agents. Solubility also has to be low enough not to cause leaching of the inhibitor, or blistering and delamination which may lead to the degradation of the coating as well as loss of its hydrophobicity. On the other hand, too high solubility values increase the conductivity of the solution among other things, which accelerates corrosion.

Benzilates are expected to be promising complexing agents primarily for use in synergistic corrosion inhibitor formulations. The primary reason for this consideration was the relatively lower solubility of benzilates compared to gluconates for instance, which lead to optimum corrosion protection since most of the inhibitor formulations could inhibit corrosion eventually by precipitating on anodic and cathodic sites, where further corrosion reactions are blocked.

First step of this process; synthesis and characterization is completed successfully in general. Exceptions were amorphous phases of some products not suitable for use as corrosion inhibitors. Successful syntheses of crystalline products instead of the amorphous ones could lead to the structural identification of these products using techniques such as X-ray diffraction.

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