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HOMOBIMETALLIC FERROCENE DERIVED FROM 1,4-phenylenebis(1*h*-1,2,3-triazole-4,1-diyl))diphenol AS BURNING RATE CATALYST

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ABSTRACT

To comprehend the synergistic catalytic effect on the thermal decomposition of ammonium perchlorate (AP) when two ferrocene (Fc) fragments are in the same molecule linked by the ligand 4,4'-(1,4-phenylenebis(1*H*-1,2,3)-triazol-4,1-diyl))diphenol (**1**) was synthesized a bimetallic ferrocene compound (**2**), and compared with other homo- and monobimetallic ferrocene compounds already reported, as a potential burning rate catalyst. We conducted a differential scanning calorimetry (DSC) analysis of compound (**2**), which showed a decrease the high-temperature decomposition (HTD) of Ammonium Perchlorate (AP) to 379 ºC. Our results suggest that the ferrocene is a suitable and competitive alternative to be used as an enhancer of solid composite propellants.

Keywords: *Thermal Decomposition, Burning Rate Catalysis, Composite Solid Propellant*.

1. INTRODUCTION

Burning rate modifiers (BRM) are commonly used to increase or decrease burning rates of solid rocket propellant. Those that increase burning rate are known either as a burn rate enhancers (BRE) or burn rate catalysts (BRC) [1]. The number of studies on the interaction of these additives with ammonium perchlorate (AP) published per year over the last 2 decades has increased by a considerable order of magnitude, as shown in the article published by Kalman [1]. Kalman describes that close to 40% of the journal articles in Scopus containing the terms AP, synthesize, with catalyst and/or modifier report creating new or modifying BRC or BRM, respectively. Evidently, the literature is rich with new materials (i.e., metal oxides, organometallic compounds, etc.) and still rising.

Within this variety, the ferrocene derivatives have become an indispensable component in HTPB/AP composite solid propellants owing to their extraordinary effects in enhancing the burning-rates and meanwhile bringing down pressure indexes of the propellants [2]. They are chemically compatible with the other ingredients of the propellant composition; they do not adversely affect the mechanical properties, have better microscopic homogeneities in distribution, superior ignitability of the propellant and show only a minor influence on sensitivity to impact, friction, and the aging even at high concentrations 2-5% [3]. Within these series, the bimetallic ferrocene complexes have better performances than the monometallic derivatives, thereby improving the performance of the composite solid propellant [4-7].

On the other hand, in the development of new high-performance energetic materials, nitrogen-rich heterocycles (i.e., imidazole, pyrazole, triazole, tetrazole, and 1,2,4,5-tetrazine) represent a unique class of energetic molecular frameworks, which have recently attracted significant interest in the design of energetic materials due to their high heats of formation, density, and thermal stability as compared to those of their carbocyclic analogues [8]. Therefore, considerable research efforts are focused on synthesizing molecules containing strained or caged structures and nitrogen-rich compounds with N-N and C-N bonds in their molecular backbone. These molecules are expected to derive their energy from the combustion of hydrocarbon skeleton, relief from molecular strain, and breakage of C-N and N-N bonds [9].

In the last years, the number of studies on dual-core Ferrocene derivatives has grown explosively due to their excellent catalytic performance as BR catalysts. Several authors have reported nitrogen-rich binuclear ferrocene derivatives, which presented high catalytic effects on the thermal decomposition of AP [3-4, 10]

Li and co-workers synthesized ionic ferrocenyl compounds composed of a mono- or dinuclear ferrocenyl quaternary ammonium cation paired with 5-ferrocenyl-1H-tetrazolate anions. These compounds showed considerably lower migration trends and strong catalytic efficiency [12]. The results confirmed these compounds as suitable BR catalysts featuring high thermal stability and accelerating decomposition behavior for AP during combustion.

In this context, especially bimetallic complexes, offer a unique opportunity to study their catalytic properties on the thermal decomposition of AP, which has a close relationship with the combustion process of the propellants. Therefore, this article aims at the one hand to obtain new catalyst for highly efficient combustion and on the other, overcome the disadvantages generated by the migration of those to date reported.

2. EXPERIMETAL PART

2.1 General Information

Unless specified otherwise, all manipulations were carried out within a dry box equipped with a Dry-Train cleaner Model HE493 and a vacuum line, using Schlenk-tube techniques under an inert atmosphere of dry nitrogen. Anhydrous solvents were distilled and dried under a nitrogen atmosphere from Na/benzophenone for tetrahydrofuran (previously distilled from AlLiH4), toluene, and hexane, and freshly distilled from P_2O_5 in the case of CH_2Cl_2 [12]. Elemental analyses (C and H) were made with a Fissions EA 1108 microanalyzer. ^{1}H NMR spectra were recorded on Bruker AC-400 and Bruker AC-200P spectrometers. Chemical shifts were reported in ppm relative to residual solvents.

The DSC analysis was conducted using a Perkin Elmer DSC 4000 instrument with a heating rate of 5 °C min^{-1} under nitrogen atmosphere, ranging from 140 to 445 °C, using 40 µL aluminum pans with a pin on the bottom. The aim was to evaluate the catalytic performance of the homobimetallic compound on the thermal decomposition of AP. The catalytic performance of the complex [Fc-L-Fc] on the thermal decomposition of AP was investigated by adding the catalyst to AP in 5 wt% (average sample mass: 5.430 mg). Analytically pure grade AP with a particle size of 200 µm was purchased from SNPE Propulsion, Groupe SNPE.

The synthesis procedure of the following compounds has been reported previously, acylferrocene [13], and 4-Azidophenol [14]. Ferrocene, 1,4-diethynylbenzene, sodium azide, sodium nitrite, and sodium ascorbate (purchased from Aldrich, Fc).

2.2 Synthesis Ligand 4,4'-(1,4-phenylenebis(1*H*-1,2,3-triazole-4,1-diyl))diphenol. (**1**)

In a reactor, 500 mg (3.7 mmol) 4-azidophenol, 233 mg (250 uL, 1.85 mmol) of phenylacetylene, 46 mg of $CuSO_4(H_2O)_5$ and 109 mg of Sodium ascorbate were loaded. After dissolving the mixture in DMF (25 mL), 5 mL of H_2O was added. After 48 h of constant stirring, the reaction crude was poured into 50 mL of H_2O and filtered under vacuum. The resulting product was washed with hot MeOH 3 times and then dried under vacuum at 50 °C for 24 h, obtaining 400 mg of a brown solid (Yield: 54.54%).

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Anal. Calc. for $C_{22}H_{16}N_6O_2$ (396.41): C, 66.66; H, 4.07; N, 21.20; O, 8.07. Found: C, 66.51; H, 4.12; N, 21.27; O, 8.10.

^{1}H NMR (400 MHz, DMSO-d_6): δ 9.94 (s, 2H), 9.17 (s,2H), 7.92 (d, 2H), 7.67 (t, 4H), 7.58 (d, 2H), 6.99 (d, 2H).

^{13}C NMR / not found.

2.3 Synthesis homobimetallic Ferrocene compound derived from 1,4-phenylenebis(1H-1,2,3-triazole-4,1-diyl))diphenol (**2**).

In a Schlenk reactor, 250 mg (0.63 mmol) 1 equiv. of **1**, 2.5 equivalent of acylferrocene and 3 equivalent of trimethylamine, under a N_2 atmosphere, maintaining the temperature at 5°C, using a mixture of dichloromethane and THF 1:1 (30 mL) as solvent. Subsequently, the mixture was refluxed for 12 h. After cooling the system to room temperature, the crude reaction was poured into Ice (50 g), and then the precipitate obtained was filtered, which was washed with acetone and dried under vacuum, obtaining 221 mg (0.27 mmol) of a red solid. (Yield: 42.50%)

Anal. Calc. for $C_{44}H_{32}Fe_2N_6O_4$ (820.47): C, 64.41; H, 3.93; N, 10.24; O, 7.80. Found: C, 64.51; H, 4.12; N, 21.27; O, 8.10.

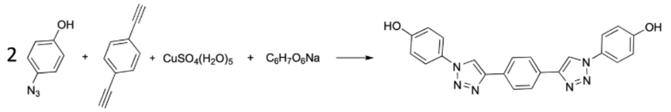
^{1}H NMR (400 MHz, DMSO-d_6): δ 9.00 (s, 2H), 7.63 (s,2H), 7.50 (s, 4H), 6.88 (s, 4H), 6.75 (d, 2H), 4.25 (s, 2H), 4.14 (s, 10H), 4.10 (s, 4H).

^{13}C NMR / not found.

3. RESULTS AND DISCUSSION

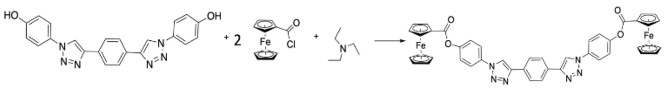
The versatile nature of ferrocene-based 1,2,3-triazolyl compounds also allows for structural modification and functionalization, enabling the design of tailor-made molecules with desired properties. By tuning the substituents on both the ferrocene and triazole moieties, it is possible to modulate these compounds' electronic, steric, and physicochemical properties, further expanding their potential applications [3-4, 10].

Compound (**1**) was synthesized by click reaction, obtaining yields of 54%. Compound (**1**) has low solubility in DMSO and is insoluble in other conventional solvents (Scheme 1).



Scheme 1: Synthetic route the bridging ligand 4,4'-(4,4'-(1,4-phenylene)bis(1*H*-1,2,3-triazole-1,4-diyl))diphenol.

Considering that the ferrocene-type complexes have been reported to be effective catalysts on the thermal decomposition of AP, this prompted us to test the activity of compound (**2**) as burning rate catalysts on the thermal decomposition of AP. Compound (**2**) was synthesized by the Fischer esterification reaction, obtaining a yield of 42.5%. Similarly to the ligand compound (**1**), compound (**2**) has low solubility in DMSO and is insoluble in other conventional organic solvents (Scheme 2).



Scheme 2: Synthetic route homobimetallic compound (**2**).

For the NMR analysis, the samples were prepared in DMSO-d_6, and the spectra were collected at 140º C due to the poor solubility of the triazoles. No signals were identifiable when the spectra were measured at room temperature because the triazoles were insoluble. On the other hand, when the spectra were collected at 140º C, consistent signals were appreciated, and, in all cases, the number of signals was coherent with the molecular structures. Compound (**1**) can be observed in the ^{1}H NMR spectrum (Figure 1), which shows signals at δ 9.94 ppm corresponding to the hydroxyl (OH) proton of phenol usually appears in the range of 9.5 to 12.0 ppm. The triazolyl group proton appears at 9.17 ppm. The signals at 7.92 – 6.99 ppm which can be attributed to the aromatic protons.

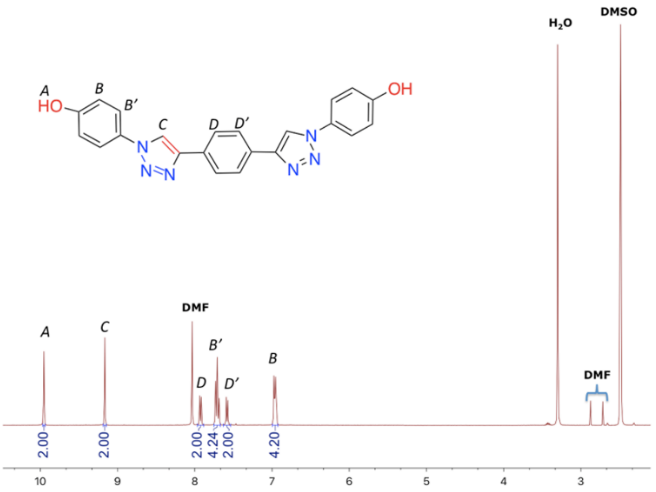


Figure 1: ^{1}H-NMR spectrum of 4,4'-(4,4'-(1,4-phenylene)bis(1H-1,2,3-triazole-1,4-diyl))diphenol, Compound (**1**), in DMSO-d_6.

For compound (**2**) can be observed in the ^{1}H NMR spectrum (Figure 2), which shows signals at δ 9.00 ppm corresponding to the triazolyl group proton and, in the same way as compound (**1**), the signals of aromatic protons are observed at 7.63 – 6.75 ppm. The signals at δ 4.25 − 4.10, and 4.10 ppm correspond to protons of the ferrocene moiety, signals similar to those previously published by our research group and other authors [10, 15]. The disappearance of the signal at 9.94 ppm is also indicative that compound (**2**) has been generated through the Fischer condensation reaction.

Unfortunately, ^{13}C NMR spectrum is not given due to the low solubility of compound (**1**) and (**2**) in deuterated DMSO solvent.

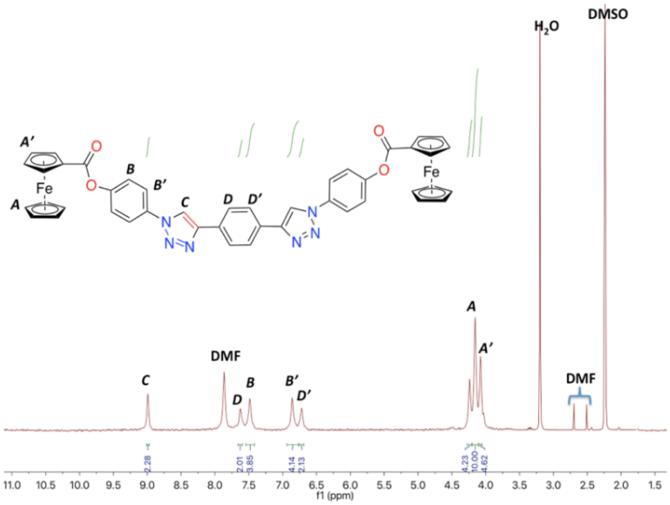


Figure 2: ^{1}H-NMR spectrum homobimetallic Ferrocene, Compound (**2**), in DMSO-d_6.

Due to the combustion effect of a BR catalysts candidate on the combustion behavior of the composite propellants is usually assessed by its effect on the thermal degradation of AP. It has been reported that ferrocene derivatives as BR catalysts give rise to a shift in the peak temperatures of AP left, accelerating AP decomposition [1-7, 10-11]. In general, the catalytic activity of a BR catalyst in composite solid propellant can be assessed by studying its effect on the thermal degradation of AP by TG and/or DSC instruments, and the mass percentage of ferrocene-based BR catalyst in AP were generally 1-5% [1-7, 10-11], in this work, 5 mass% of catalyst was used.

As mentioned above, Triazole compounds have been studied for their potential as energetic materials and burn rate modifiers due to their structural features and reactivity. These compounds can act as energy-dense components and may contribute to the overall combustion process [8]. In this sense, the performance on the thermal degradation of the AP of the compound (**1**) and its bimetallic ferrocene derivative (**2**) as a combustion rate catalyst have been carried out and is shown in Figure 3.

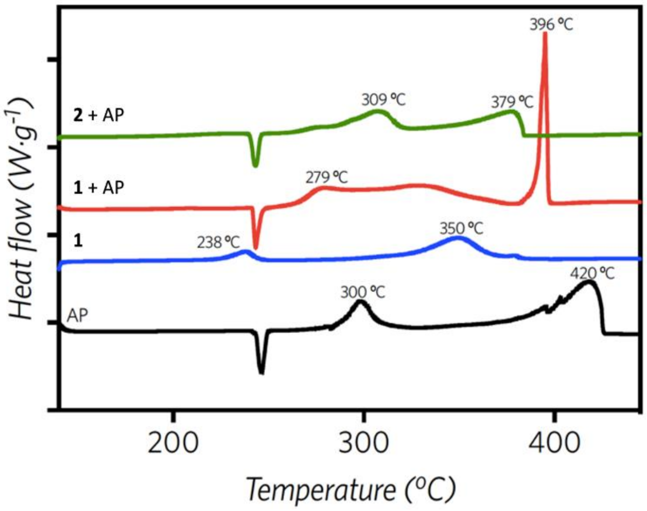


Figure 3: DSC curves of the catalytic performance for AP pure and mixture of compound (**1**) and its bimetallic ferrocene derivative (**2**) with AP at 5 wt %.

As has been described in literature, the DSC curve of the thermal decomposition of AP show three processes (Figure 3 - black line), an endothermal and two exothermic processes. As is known, the orthorhombic to cubic crystal stage transition occurs at 248°C and is associated with the endothermal peak. The first exothermic process corresponds to the low-temperature decomposition (LTD) (292°C), which is accepted by several authors to be associated with an electron transfer between ammonium and perchlorate ions, and the second exothermic peak is related to the high-temperature decomposition (HTD) step at 420°C [16].

The DSC curve of the thermal decomposition of compound (**1**) was carried out in order to observe the decomposition processes and be compared with the AP (Figure 3 – blue line). The blue line shows that compound (**1**) has two decomposition temperatures at 238 ºC and 350 ºC in the range studied.

The specific mechanisms by which triazole compounds function as burning rate catalysts can vary and often depend on the particular structure of the triazole derivative. Triazoles may participate in the combustion process by releasing gas, influencing the thermal stability of the formulation, or affecting the decomposition pathways, as observed in the mixture between compound (**1**) and AP at 5% by mass (Figure 3 – red line). Compound (**1**) produces a shift to the left of the HTD of AP at 24 ºC, this suggests that the incorporation of triazole compounds into these formulations could influence the combustion characteristics, making the reactions more efficient or controlling the rate of combustion, due the exothermic peak become sharper, indicating the decomposition process of AP becomes more quickly [5].

On the other hand, ferrocene-based compounds have been explored as burning rate catalysts in the field of propellants and energetic materials [3]. When extended to bimetallic systems, these compounds may exhibit enhanced catalytic effects on the burning rates of propellants [4-7]. The utilization of these complexes as burning rate catalysts is part of ongoing research efforts to optimize the performance of energetic materials. From the result obtained from the mixture of "AP + Compound (**2**)" at 5% by mass, compound (**2**) showed a greater change in the HTD of AP at 41 ºC (Figure 3 - green line), similar to some catalysts derived from ferrocene already informed [1-7, 10-11], indicating that the bimetallic complex (**2**) has a better catalytic effect on the thermal decomposition of AP vs. the organic compound (**1**).

CONCLUSION

This study investigated the synthesis, characterization, and catalytic properties of compounds (**1**) and (**2**). The synthesis of the compounds was achieved through click and Fischer reactions respectively, with moderate yields (54−43%).

Compound (**1**) was more active among the complexes here reported, shifting to the left the HTD of AP in 41ºC. Research in this area aimed to design bimetallic ferrocene-based compounds with tailored properties to optimize their performance as burning rate catalysts, however, the effect of BR catalysts cannot only be focused on the influence on the thermal decomposition of AP. The results confirm the compounds derived from 1,4-phenylenebis(1H-1,2,3-triazole-4,1-diyl))diphenol could have potential applications as burning rate catalysts in composite solid propellants. In this way, using derivatives of the triazole compounds opens new horizons to explore combustion catalysts, which propellants and explosives continue to explore and optimize the use of various compounds, including triazoles, to improve the efficiency and safety of these materials.

Researchers in the field of propellants and explosives continue to explore and optimize the use of various compounds, including triazoles, to improve the efficiency and safety of these materials.

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