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Research paper

Synthesis, anti-migration properties and burning rate catalytic properties of ferrocene-based compounds



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ARTICLE INFO	ABSTRACT
<i>Keywords:</i> Burning rate catalyst Ferrocene-based hydroquinone compounds Anti Migration behavior	Five ferrocene (Fc)-based compounds (HQ-Fcs) were synthesized by the condensation reaction of ferrocene- carbonyl chloride with corresponding hydroquinone derivatives. Nuclear magnetic resonance (¹ H NMR), and Fourier transform infrared (FT-IR) were used as evidence for the synthesis of HQ-Fcs . The electrochemical properties of HQ-Fcs were investigated by cyclic voltammetry (CV) and suggested that these compounds ex- hibited redox behavior due to ferrocene groups. The burning rate catalytic effect of HQ-Fcs was examined by Thermogravimetric (TG) and differential Thermogravimetric (DTG) techniques. Thermal analysis results in- dicated that HQ-Fcs were thermally stable and have better burning rate catalytic effects in accelerating thermal decomposition of AP. Anti-migration behavior of HQ-Fcs in comparison to commonly used 2,2-bis (ethylfer- rocenyl) propane (catocene) and Fc was evaluated. It was observed that HQ-Fcs delivered excellent anti-mi- gration performances than catocene and Fc.

1. Introduction

Fc one of most well-known organometallic compounds, is an electron-rich aromatic complex having ferrous ion sandwiched by cyclopentadienyl rings and has emerged as a subject of intensive research worldwide in recent times [1-4]. Fc and its derivatives due to their inherent

thermal stability, aromaticity, low toxicity, lipophilicity, reversible redox behavior and modification possibilities [5-8] are highly fascinated, therefore they have gained increasing applications in different fields such as catalysis, medicinal chemistry, non-linear optics, materials science, electrochemical sensing, memory storage, nano-materials, biologically active compounds and ion recognition [9-14]. Owing to excellent catalytic features, numerous ferrocenylated derivatives and compounds are well recognized BRCs for solid propellant systems [15,16]. Among all the BRCs, Fc based BRCs from viewpoint of their microscopic homogeneities in distribution, low pressure exponents, good compatibility with organic binder, broad range of BR adjustment and better ignitability in solid propellants are considered to be superior and have extraordinary effects in elevating the burning rates of solid propellant [15,17–20]. Although BRCs from Fc family are favorable in enhancing burning rate and exhibiting catalytic effect for the thermal decomposition of ammonium perchlorate (AP) in solid composite

propellants [21], BRCs from Fc still pose some serious disadvantages. The main shortcoming of these Fc-based BRCs arises from their high migration tendency on prolong storage, sublimation loss during processing and phase separation by crystallization [22-24]. These setbacks leads to the destruction of designed parameters, shortens the service life of the propellant, reduces resistance to aging by forming sensitive boundary layers and may cause dangerous explosions [25-27]. To preclude these drawbacks and also to improve the efficiency of Fc-based BRCs it is necessary to design low migratory Fc- based BRCs [28,29].

Fc derivatives such as n-butylferrocene (NBF), tert-butylferrocene (TBF), and 2, 2-bis (ethylferrocenyl) propane (catocene) have been developed to overcome unwanted migration property. However, these molecules are volatile, thus exhibit an obvious migration to the propellant interface [30]. In recent times many efforts have been made striving for Fc-based BRCs that are less volatile as well as equipped with high catalytic activities [31]. Anti-migratory research outcomes indicated that grafting of ferrocenyl groups into either the backbones or the side chains of polymers and oligomers is an effective way for improving burning rates and mitigating migration tendency [32]. Furthermore, the migration problems of Fc-based BRCs can be overcome by: (i) extending the carbon chain length on Fc ring, (ii) introducing polar elements like oxygen and nitrogen, (iii) introduction of reactive groups such as -OH, -NH2, -NCO, etc. which can form cross-linked

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network and thus prevent volatilization and migration. (iv) introduction of inorganic groups in Fc ring and (v) synthesis of high molecular weight ferrocenyl dendrimers, containing large number of polar elements like oxygen and nitrogen [30,33,34]. Zain and co-workers developed less migratory Fc-based compounds [27].Ting Li and coworkers designed low migratory ionic compounds of ferrocenylmethyldimethylamine [30]. Luo and co-workers synthesized Fcbased hyperbranched poly(amine-ester) and hyper-branched poly (amine-ester) [35]. Although extensive efforts have been oriented to lower migration tendency and enhance the combustion catalytic activity of Fc-based BRCs. However, the problem is still being continued [36].

Hydroquinones are an important class of compounds and, surprisingly there has been limited number of work entitling the synthesis of ferrocenyl substituted hydroquinones. Herein, we have reported the synthesis of low migratory Fc-based compounds in order to solve the migration problem as well as to improve the burning rate catalytic activity in AP-based propellants. The success of synthesis was confirmed by the ¹H NMR, and FT-IR. The electrochemical properties of **HQ-Fcs** were studied by CV [37]. TG and DTG techniques were applied for investigating the thermal catalytic behavior of **HQ-Fcs**. Anti-migration behavior in AP-based propellant was investigated at 50 °C and atmospheric pressure in comparison with catocene and Fc. We investigated the effect of polar elements (oxygen) and electronegative halogen group on the anti-migration behavior of small Fc-based hydroquinone compounds [27].

2. Experimental

2.1. Materials

Hydroquinone (HDQ), tetrafluorohydroquinone (TFH), 2,5-dibromohydroquinone (DBH), hydroquinone bis(2-hydroxyethyl)ether (BEH), tetracholorohydroquinone (TCL) and tetrabutylammonium tetrafluoroborate (Bu_4NBF_4) were purchased from J&K Chemical Reagent Co. Ltd. Dichloromethane (DCM), oxalyl chloride, ferrocenecarboxylic acid, pyridine, petroleum ether, tetrahydrofuran (THF), triethylamine (TEA), chloroform, sodium hydride (NaH) and NaHCO₃ were also purchased from Sinopharm Chemical Reagent Co. Ltd.

2.2. Synthesis

2.2.1. Synthesis of ferrocenecarbonyl chloride

Ferrocenemonocarbonyl chloride was prepared in accordance with the stated procedure in literature, accompanied by slight modifications [38]. The initial step for this synthesis involved the drying of ferrocenemonocarboxylic acid (30.0983 g, 121.904 mmol) at 40 °C for 4 h under vacuum condition. Afterwards solution of ferrocenemonocarboxylic acid was formed by using freshly distilled DCM (270 mL). Pyridine (23 mL, 285.508 mmol) was injected to this ferrocenemonocarboxylic acid solution and was stirred well under argon (Ar) atmosphere at room temperature for about 15 min. Furthermore drop wise addition of oxalyl chloride (24 mL, 279.839 mmol) was carried out at room temperature. The resulting reaction mixture was at first stirred for 30 min at room temperature and then was allowed to reflux for 6 h. The content of the reaction flask was dried under vacuum and the residue was extracted using petroleum ether (100 mL) at 90 °C. The obtained ferrocenemonocarbonyl chloride was kept in Ar atmosphere [38].

2.2.2. Synthesis of HQ-Fcs

The synthetic methodology for **HQ-Fcs** involved condensation reactions of hydroquinones with ferrocenecarbonyl chloride. For the preparation of ferrocenyl hydroquinone **HDQ-Fc**, hydroquinone (1.0985 g, 9.977 mmol) was initially dried under reduced pressure and then was dissolved in 35 mL freshly distilled THF. Afterwards TEA as a deacid (3 mL, 21.509 mmol) was injected to the hydroquinone solution. The obtained mixture was kept under stirring at room temperature for 15 min. Later to this mixture ferrocenecarbonyl chloride (5.6930 g, 22.909 mmol) in solution form prepared in 35 mL freshly distilled THF was injected slowly. The resulting solution was then refluxed for 18 h. The solvent was evaporated on a rotary dryer. The obtained product was dissolved in 200 mL CHCl₃. The resulting solution was first washed (four times) with 1% NaHCO₃ solution prepared in distilled water and then further washed (three times) with distilled water. The organic layer was separated, anhydrous Na2SO4 (2.0048 g) was added and was put overnight. The mixture was filtered for the separation of Na₂SO₄ and then the obtained filtrate was dried on rotatory evaporator to get the product. The product was further dried in vacuum oven at 40 °C for 1 day. Similarly, for ferrocenvl tetrafluorohydroquinone (TFH-Fc), ferrocenyl dibromohydroquinone (DBH-Fc), ferrocenylhydroquinone-bis (2-hydroxyethyl) ether (BEH-Fc) and ferrocenyl tetracholorohydroquinone (TCL-Fc), above mentioned synthetic procedure (i.e reacting ferrocenecarbonyl chloride with corresponding hyquinones) was followed [39].

2.3. Characterization

¹H NMR spectra of the synthesized Fc-based hydroquinone compounds were recorded on AVANCE NMR spectrometer (600 MHz, Model DMX-400). For these compounds the chemical shifts were related to tetramethylsilane (TMS) at $\delta = 0$ ppm by using DMSO or CDCl₃ as a solvent. FT-IR spectra were recorded on a Nicolet 5700 infrared spectrometer by KBr pellet technique. 2% sample and KBr were crushed to a powder and mixed together and KBr pellet was prepared.

Cyclic Voltammetry was carried out on a CHI-630A electrochemical analyzer (CH Instruments, Inc., Austin, Texas) in an undivided threeelectrode cell. The concentration of the electrolyte was 0.1 M, the potential scan rates were 0.1-0.5 V/s and concentration of HQ-Fcs were 0.5 m M. The samples for anti-migration studies consisted of three adjacent parts: unloaded part (blank), interface and loaded part. These three constituents represent insulation, liner and propellant, respectively. The unloaded part consisted of AP, hydroxyl-terminated polybutadiene (HTPB) and isophorone diisocyanate (IPDI) and it was prepared by mixing them for 30 min to obtain homogeneous slurry. The resulting mixture was cast into a mold and cured at 25 °C for three days before undergoing accelerated aging. The loaded part was prepared by mixing AP, HTPB, IPDI and a BRC. Typically, sample containing HDQ-Fc was prepared by mixing AP, HTPB, IPDI and HDQ-Fc for approximately 1 h. The resulting mixture was subsequently cast on unloaded layer that had been cured for three days. After curing for three days at room temperature, the prepared sample was aged in an oven at 50 °C and atmospheric pressure for 30 days. Burning rate catalytic performance of ferrocenylated-amino pyridines and ferrocenylated-amino thiazoles was investigated with a PerkinElmer Pyris 1 thermogravimetric instrument at a heating rate of $5 \,^{\circ}\text{Cmin}^{-1}$ under nitrogen in the range 50-600 °C. The required amount (5 wt%) of ferrocenylated-amino pyridines and ferrocenylated-amino thiazoles and AP was mixed and ground.

3. Results and discussion

3.1. Synthesis and characterization of HQ-Fcs

Ferrocenecarbonyl chloride was prepared from ferrocenecarboxylic acid by following the reported literature [12]. The synthesis of ferrocenecarbonyl chloride is shown in Scheme 1.

HQ-Fcs were synthesized by the condensation reaction of ferrocenecarbonyl chloride with corresponding hydroquinones in freshly distilled THF. The experimental detail for the synthesis of Fc-based hydroquinone compounds is given in Table S1.

The structures of the synthesized compounds were characterized by ¹H NMR spectroscopy. On comparing ¹H NMR spectra of these **HQ-Fcs**



Scheme 1. The synthetic route of Fc-based hydroquinone compounds.

with corresponding hydroquinone derivatives, three new peaks (4.00–5.00 ppm) attributed to Fc protons appeared. ¹H NMR spectra of **HQ-Fcs** are shown in Fig. S1. The integration of all the peaks including peaks of Fc was according to the structures, which further supported the successful synthesis of HQ-Fcs. The spectroscopic data for **HQ-Fcs** are given in the supporting information.

The structures of Fc-based hydroquinone compounds were further confirmed by FT-IR spectroscopy. The strong vibrational and deformational bands centered at 1015–1045 cm⁻¹, 801–835 cm⁻¹ and 480–502 cm⁻¹ were the evidence of ferrocenyl groups [40,41]. The C–H vibrational stretching bands were observed around 3030 cm⁻¹, and 2960–2850 cm⁻¹ respectively. The bands around 1725 cm⁻¹ were assigned to the stretching vibrations of carbonyl esters in **HQ-Fcs** [42]. Meanwhile the stretching vibrations of esters (C–O) were found around 1073–1150 cm⁻¹ [43]. Peaks located at 1671 cm⁻¹ and 1455 cm⁻¹ were attributed to stretching vibrations of (C=C) in the newly synthesized compounds [44]. FT-IR spectra of **HQ-Fcs** are shown in Fig. S2.

3.2. Electrochemical behavior of HQ-Fcs

The electrochemical process involves loss and gain of electrons. Since the combustion process of the solid propellant also involves loss of electrons, therefore it's important to investigate the electrochemical properties of **HQ-Fcs** for figuring out their potential as BRCs. CV has been considered as effective technique for exploring redox properties of Fc based compounds instead of studying their combustion properties directly [45]. **HQ-Fcs** showed good solubility with varying polarities in different solvents, so their electrochemical properties were studied in DCM, CDCl₃, and DMSO with Bu₄NBF₄ (0.10 M) as a supporting electrolyte at 20 °C. The results of CV curves for **HQ-Fcs** are shown in Figs.

S3–S7 and the numerical information is given in Table S2. The electrochemical results indicated that the solvent polarity as well as the potential scan rate has high impact on redox properties of **HQ-Fcs**. The change in polarity of the solvent affected the shape of CV curves and it has been observed that the increase of solvent polarity resulted in deformation of the peak shapes. The peaks were found to be more distorted in case of highly polar DMSO. The high viscosity of DMSO offered greater resistance to ion movement therefor resulted in multiple redox peaks. Both oxidation and reduction peaks potential was decreased with the increase in polarity of the solvent, which showed that polarity of solvent was proportional to reduction and oxidation processes for **HQ-Fcs**.

The most well-defined and sharp peaks were obtained in DCM and $CHCl_3$ with high current in DCM. The appearance of single oxidation and reduction peaks indicated the equal behavior of ferrocene in terms of electronic transfer between Fe^{2+} and Fe^{3+} .

HQ-Fcs was also found sensitive to various scan rates in organic solvents. Increase of scan rate led to increase in peak current values (i_{pc} and i_{pa}). According to CV theory, these results show that charge transport of the electrode processes obeyed Fick's law at room temperature. The rate of electrode reaction was found to be fast in DCM. The redox reactions were smooth in DCM due to little solvent resistance and faster charge diffusion rate.

The measurements, carried out in an organic solvent (DMSO), observed to be in the range of 386–443 mV for $Ep^{1/2}$ and 77–108 mV for ΔE_p seemed adequate, indicative of an quasireversible ferrocene/ferrocenium wave. Peak to peak potential separation (ΔE_p) was found to be larger in CHCl₃ and smaller in DCM, while the rate of electrode reaction decreased from DCM to CHCl₃.

The ferrocenes substituted compounds showed greater redox

potentials, indicating the oxidation of new compounds more difficult than the neutral ferrocene derivatives and exhibit higher anti-oxidative ability under similar conditions. For **TFH-Fc**, **TCL-Fc** and **DBH-Fc** the electronic density decreases over the iron center and the 2 + oxidation state of the iron ion is more stabilized by the electron-withdrawing effect of the halogen groups. The shielding of the iron atom by the carbonyl group in **HDQ-Fc** render the interaction of the iron atom with the electrode difficult, thereby increasing in the positive charge on the iron atom and hence reduced. The lesser electron–withdrawing effect of substituents results in greater stabilization of the 3 + oxidation state of the metal for **BEH-Fc** [32,46–48].

3.3. Anti-migration studies of HQ-Fcs

Anti-migration performances of HQ-Fcs were tested against catocene and Fc under the same aging conditions. Sample preparation details of anti-migration studies are given in Table S3 and the procedure adopted for the assembly of migration tube is shown in Fig. S8.

For both Fc and catocene obvious migration was noticed as they start migrating even after 7 days storage, whereas **HQ-Fcs** showed much slower migratory behavior than catocene and Fc. After 30 days negligible migration was found in case of **HQ-Fcs**. The reason to this excellent anti-migration behavior was perhaps, the van der Waals forces between the propellant and **HQ-Fcs**. These forces were caused by the presence of oxygen atoms in these compounds. Non-migratory results observed in case of **HQ-Fcs** due to their more polar and electronegative nature is shown in Fig. S9 and their migration distances are plotted in Fig. 1. Based on the anti-migration trends, migration mechanism was proposed (Fig. 2).

It indicated Fc to be a small and highly volatile molecule as its migration appeared after short aging period and reached to the ends of the tube while **HQ-Fcs** were stable, less volatile and presented decent anti-migration ability, probably due to their higher molecular weights. The presence of oxygen atoms attached with carbonyl groups contributed towards the formation of dipole-dipole forces and hydrogen bonding which binds **HQ-Fcs** and the propellant providing hindrance against migration.

3.4. Burning rate catalytic performance and possible catalytic mechanism of *Fc*-based compounds

For BRCs thermal stability is considered as significant parameter







Fig. 2. Migration mechanism: (a) **BEH-Fc** with migration model of **BEH-Fc** and (b) ferrocene with migration model of ferrocene.

and thermally stable BRCs are perceived to encourage the steady combustion of a solid propellant. Since AP is key component and its thermal decomposition behavior is related to the combustion behavior of the propellants in solid propellant. Therefore the burning rate catalytic activity of a Fc-based BRC is often judged by investigating its effect on the thermal decomposition of AP [21]. The burning rate catalytic effect of **HQ-Fcs** for the thermal degradation of AP was determined by TG and DTG techniques using 5 wt% mixture of the **HQ-Fcs** with AP. Fig. 3(a) and (b) presents the results of conducted thermal studies.

The catalytic efficiency of **DBH-Fc** for the thermal degradation of AP was also studied by varying the content (1-5 wt%) of **DBH-Fc**, shown in Fig. 3(c) and (d). The detail of samples preparation for thermal analysis and catalytic performance is given in Table S4.

From the TGA results, it was observed that the thermal decomposition of AP was around 445.27 °C, but the addition of specific amount of **HQ-Fcs** (5 wt%) in AP evidently shifted the decomposition peaks forward towards the left, thereby indicating positive effect in accelerating **HQ-Fcs** were found thermally stable up to 220 °C and presented the best catalytic behavior by lowering the thermal degradation temperature of AP around 351.17 °C. Furthermore Fig. 3(c) indicated that the increase in wt% of **DBH-Fc** resulted in decreased thermal disintegration temperatures of AP. This could be due to increasing concentration of Fc, which is considered to have efficient catalytic effect in promoting fast decomposition of AP.

DTG curves in Fig. 3(b) showed that pure AP and mixtures of HQ-Fcs with AP were decayed over two stages. First stage decomposition was related to low temperature decomposition (LTD) where the partial decomposition of AP occurred, while second stage where complete decomposition of AP took place corresponded to high temperature decomposition (HTD). For pure AP, LTD was observed at 341. 42 °C and HTD was observed at 432.94 °C, while in the case of HQ-Fcs, LTD was around 300–330 °C and HTD appeared around 350–390 °C. The maximum weight loss was for 5 wt% DBH-Fc (Fig. 3b).With increase in wt% of DBH-Fc, the decomposition of AP become rapid (Fig. 3d). The drastic decrease in both LTD and HTD indicated HQ-Fcs to have effective and



Fig. 3. (a) TG curves of pure AP and AP with 5 wt% of HQ-Fcs, (b) DTG curves of pure AP and AP with 5 wt% of HQ-Fcs, (c) TG curves of pure AP and AP with 1–5 wt% of DBH-Fc (d) DTG curves of pure AP and AP with 1–5 wt% of DBH-Fc.

accelerating catalytic effect on thermal decomposition of AP.

The catalytic mechanism of **HQ-Fcs** in AP-based propellant can be explained in terms of thermal decomposition of AP. The covalently bonded hydroquinone structures having polar elements show anti-migration properties while ferrocene contributes in the burning rate catalytic properties.

3.5. Possible burning rate catalytic mechanism of ferrocene-based compounds on the thermal decomposition of AP

Fc-based polymers, and their derivatives have high redox potential (E_{red}) and their E_{red} value depends upon the nature of the substituent on the ferrocene ring [40,49]. But still the burning rate catalytic mechanism of Fc-based polymers, and their derivatives is not clear [17,50]. Four catalytic mechanisms namely: electron transfer mechanism, proton transfer mechanism, forming transition materials mechanism and acid–base interaction have been proposed [51]. The burning rate catalytic mechanism of Fc-based compounds in AP-based propellant can be explained in terms of thermal decomposition of AP [15]. The incorporation of ferrocenylated compounds leads to accelerated decomposition of AP through electron transfer mechanism [17]. The electron-withdrawing halogen substituents of ferrocene compounds may promote the decomposition process of AP by removing

electron density from the ring [47,52]. It can be noticed for HDQ-Fc to have the lower decomposition peak temperatures for AP at around 346.17 °C corresponding to their oxidation potential. The results suggested that the ultimate decomposition temperatures of AP with HDQ-Fc as additive was lower than the others, implying good effects of HDQ-Fc as BRC. It has been accepted that ferrocenyl derivatives tend to form Fe₂O₃ particles. Dinuclear ferrocenylated compounds are supposed to be firstly burnt up, producing Fe₂O₃ nanoparticles and the distance between the two iron atoms is suitable for the formation of Fe₂O₃ nanoparticles, which are strong promoter in the gas phase to accelerate the decomposition of AP [16,53]. Due to fact that the Fe atoms of HDQ-Fc are located nearer than that of BEH-Fc, the AP decomposition peak temperature catalyzed by HDQ-Fc was lower than that of BEH-Fc.

The thermal decomposition mechanism of AP can be presented in two ways (i) electron transfer process in AP decomposition, which can be catalyzed by an additive, and (ii) the rupture of the chemical bond in ClO₄ of AP [54]. **HQ-Fcs** maintain redox properties and initiated the decomposition by electron transfer process of ferrocene/ferrocenium in ferrocene groups. The redox potential of these **HQ-Fcs** presented by their low oxidation potentials in comparison to ammonium perchlorate was more helpful to accelerate the decomposition and shifted the AP peaks towards lower temperatures, corresponding to the possibility that the Fe²⁺ in Fc is oxidized into Fe³⁺ by AP and then reduced into Fe²⁺ by NH₃ produced by the degradation of AP at high temperature and the charge balance of AP is destroyed, which promotes the degradation rate of AP. Thus, the thermal decomposition of AP takes place through an electron transfer process below 300 °C. [41]. Ferrocenyl derivatives are supposed to be firstly burnt up, transforming Fe₂O₃ particles [28] with a large surface area above 300 °C [32]. The Fe₂O₃ particles might absorb ClO₄ in its gas phase to catalyze the rupture of the chemical bond in AP. Hence, both the electron transfer process and the catalytic decomposition effect of Fe₂O₃ particles can play key roles in AP decomposition. Zain-ul et al. [55], Tong et al. [56] and Povea et al. [16] gave a more visual description of the burning process. Since combustion is essentially a drastic oxidation-reduction process and also is a complex redox reaction, the combustion of composite solid propellants presents complications, preventing a thorough understanding of its progress. Based on references [17,28,52-55], the combustion of AP-based propellant containing ferrocene-based compounds results in formation of nanoscale Fe₂O₃ fine particles. These nanoscale Fe₂O₃ fine particles have larger surface area and show excellent burning rate catalytic activity in thermal decomposition of AP [17,28,56,57].

4. Conclusion

Five Fc-based hydroquinone compounds have been synthesized and confirmed by ¹H NMR and FT-IR spectra. The electrochemical investigation indicated that **HQ-Fcs** showed redox behavior due to the presence of Fc. Anti-migration studies indicated that due to the presence of oxygen, these **HQ-Fcs** showed better anti-migration properties. This could be attributed due to the formation of dipole-dipole interactions. TG and DTG results indicated that **HQ-Fcs** showed good catalytic performance on the thermal decomposition of AP.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ica.2019.118958.

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