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Synthesis, characterization, migration and catalytic effects of energetic ionic ferrocene compounds on thermal decomposition of main components of solid propellants

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ABSTRACT

Sixteen new energetic ionic ferrocene compounds, $[FcCH_2N(CH_3)_2(C_nH_{2n+1}]^+X^-$ (Fc = ferrocenyl; X^- = nitrate or picrate anion; n = 3–10), were synthesized in high yields and characterized by ^1H NMR, ^{13}C NMR, UV–Vis, elementary analysis, TG and DSC methods. All the compounds show high thermal stability. Cyclic voltammetry investigations revealed that the ionic compounds exhibit redox waves for ferrocenyl groups and are considered as irreversible redox systems. Migration studies disclosed that their migration tendency increases with elongation of alkyl chain length in the cations of the compounds, and much slower than that of neutral *n*-butylferrocene (NBF). The sensitivities tests towards impact and friction revealed that all picrates are sensitive compounds, while the nitrates are less sensitive analogs. Their catalytic performances for thermal degradation of main components of solid propellants such as ammonium perchlorate (AP), 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX), 1,2,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX) and hydroxyl-terminated polybutadiene (HTPB) as well as 1:1 mixture of HTPB and AP, were evaluated by DSC and/or TG techniques. All the ionic compounds can efficiently catalyze the thermal degradation of AP, HTPB and their 1:1 mixture. Compounds **1**–**8**, **11** and **16** exhibit catalytic activity in thermal decomposition of RDX. None of them display distinct catalytic effect on the thermal degradation of HMX. These low-migration ferrocene derivatives may be used as alternatives to NBF in HTPB/AP composite solid propellants.

1. Introduction

Ferrocene derivatives have been paid much attention since ferrocene was firstly reported in 1950th [1]. They generally have high thermal stabilities, good reversible redox behaviors and were found extensive applications in many fields of chemistry and material science. One of their applications is in the hydroxyl-terminated polybutadiene (HTPB) propellants containing ammonium perchlorate (AP) and Al powder as burning-rate (BR) catalysts [2–4]. Although ferrocene-based BR catalysts have extraordinary effects in the enhancement of the burning rates of HTPB/AP composite propellants, they have some disadvantages such as easy migration from propellant grain to insulation during storage, and distinct evaporation and sublimation during processing [2–4]. Moreover, the curing process of a ferrocene-based BR catalyst, 2,2-bis(ethylferrocenyl)propane (Catocene), with ultra-fine ammonium perchlorate (AP) may cause explosion [4]. Many efforts were therefore devoted to develop new ferrocene-based BR catalysts with low migration tendency. A number of azole-based dinuclear ferrocene derivatives were synthesized in recent years and they showed significant catalytic effect on thermal decomposition of AP [5–8]. French dynamite company developed butacene, which is a HTPB binder with ferrocene groups hanging on its molecular chain [9]. Grafting ferrocene units onto the side chains of HTPB increased burning rate of solid propellants and also reduced the mobility. Incorporating ferrocene units into the binder backbone during curing [2] or grafting ferrocene unit onto hyper-branched structures [10,11] are also effective ways to improve burning rates and retard the migration trend. Additionally, diverse ferrocene derivatives containing functional groups prone to polymerization have also been reported, their high costs and bad processibility, however, prevented their potential applications [12–15]. Although extensive efforts have been oriented to enhance the combustion

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catalytic activity and meanwhile to lower migration tendency of ferrocene-based BR catalysts, the problems still impeded their applications as BR catalysts in composite solid propellants [2–4,16–19].

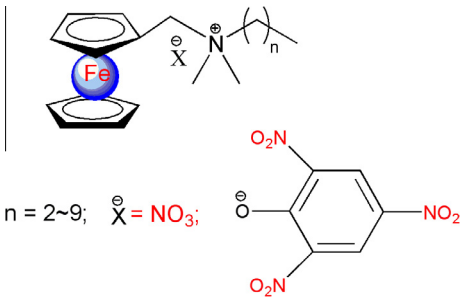
In the last decades, energetic ionic compounds have been extensively studied for their unique properties such as low vapor pressures, high densities, high heats of formation, high thermal stability, etc., compared to their atomically similar non-ionic analogs [20–25]. And another property is their easy design and modification. Motivated by the unique properties of energetic ionic compounds, we designed and synthesized a number of new ionic quaternary alkyl ammonium type mono- and dinuclear ferrocene compounds with nitrogen-rich anions such as nitrate, picrate and polynitriles by means of the synthetic strategy of energetic ionic compounds, aiming to lower the migration rates of neutral ferrocene analogs meanwhile increase the energy level of the propellants. Herein we report sixteen ionic mononuclear ferrocene compounds with nitrate or picrate as anions (Scheme 1).

Since AP is the principal component in HTPB/AP composite propellants formulation, its contribution to the thermal decomposition of propellants is usually significant. The combustion catalytic activity of ferrocene-based BR catalysts is normally evaluated for their effects on thermal decomposition of AP. Generally, high percentage of AP (~68%) and Al powder (18–20%) in HTPB/AP propellants is a disadvantage for missile stealth due to intensive exhaust produced by rocket motor during combustion process of the propellants. Nitroamino-compounds such as 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX) or 1,2,5,7-tetranitro-1,3,5,7-tetraaza cyclooctane (HMX) may be used for partial substitution of AP in order to design smokeless propellants. However, lower heat released by RDX and HMX during combustion impeded their applications in HTPB/AP composite propellants. For developing high burning rate and low-migration BR catalysts for composite propellants, the combustion catalytic activity of the new ionic ferrocene compounds in thermal degradation of AP, RDX, HMX and HTPB were evaluated and their migration tendency in solidified HTPB was also determined.

2. Experimental

2.1. Materials and equipment

AP, RDX, HMX and HTPB are provided by Xi'an Modern Chemistry Institute. N,N′-dimethylmethylferrocene was purchased from Meryer (Shanghai) Chemical Technology Co., Ltd and both $CH_3(CH_2)_nI$ (n = 2–5) and $CH_3(CH_2)_nBr$ (n = 6–9) from Alfa Aesar (Tianjin) Chemicals Co. Ltd. Additional reagents and chemicals in this work were of AR grade and used as received. All (ferrocenylmethyl)dimethylalkylammonium iodides and bromides were synthesized according to the synthetic procedures for binuclear ferrocene compound N,N′-bis[(ferrocenylmethyl)dimethyl] dodecylenediammonium diiodide described by Yamamoto [26]. FT-IR spectra were performed on an EQUINX 55 spectrometer in KBr matrix. ^1H and ^{13}C NMR spectra were recorded on a Bruker Advance 400 MHz spectrometer. Elemental analyses were carried out with a Vario EL III Elemental Analyzer, Germany. DSC and TG studies were undertaken on a HS-1 model from Beijing Henven scientific instrument factory and a Q50 model from TA company of USA, respectively, operating at 5 °C min^{-1} in nitrogen atmosphere (50 mL min^{-1}) with open Al_2O_3 sample pan. Low-temperature DSC data for compounds **15** and **16** were obtained on a Q1000DSC+LNCS+FACS Q600SDT thermoanalyzer system from TA Company of USA. Sample masses for both TG and DSC tests were in the range 1–3 mg to prevent the damage to the instruments. Combustion catalytic properties of the ferrocene ionic compounds for thermal decomposition of the principal components of solid propellants were assessed by DSC and TG techniques. UV–Vis adsorption spectra were recorded on a UV-2450 spectrophotometer of Shimadzu Corporation, Japan. Cyclic voltammograms were recorded with an CHI660C analyzer. Redox potentials were measured at a scan rate of 100 mV s^{-1} in CH_3CN containing 0.1 mol L^{-1} n-Bu_4PF_6 as the supporting electrolyte. An Ag/Ag + reference electrode and a platinum working electrode were used. The test samples for migration studies were prepared according to the reported procedure [27]. The sensitivities of the ionic ferrocene compounds towards impact (IS) and friction (FS) were determined with a WL-1 fall-hammer and a WM-1 pendular friction tester, respectively.



Scheme 1. Molecular structures of (ferrocenylmethyl)alkyldimethylammonium nitrates and picrates.

2.2. Synthesis

2.2.1. General procedure for synthesis of the ionic ferrocene compounds

Since the synthetic procedures for all the compounds are similar, the preparation process for (ferrocenylmethyl)propyldimethylammonium nitrate (**1**) was taken as an example. To a 100 mL Schlenk flask containing 2.06 g (5.0 mmol) (ferrocenylmethyl)propyldimethylammonium iodide in 30 mL methanol was added dropwise 1.02 g (6.0 mmol) of $AgNO_3$ in 30 mL methanol with stirring under nitrogen atmosphere. A yellow precipitate was formed immediately and the stirring was continued for another 2 h. The suspension was filtered through a pad of celite and evaporated to dryness and the residue was redissolved in methylene dichloride and filtered. The filtrate was evaporated to dryness and recrystallized from methanol/diethyl ether and a yellowish powder was afforded at 40 °C for 24 h under vacuum.

*2.2.1.1. Data for (ferrocenylmethyl)propyldimethylammonium nitrate (**1**).* Yellow powder, Yield: 1.43 g (82.3%). m.p.: 138.1–140.2 °C. *Anal.* Found: C, 55.13; H, 6.79; N, 8.14. Calcd.: C, 55.19; H, 6.95; N, 8.04%. IR(KBr): cm^{-1}, 3093m, 3031m, 2972m, 2360m, 1475m, 1348vs, 1236m, 1101m, 1039m, 997m, 854m, 823m. ^1H NMR (400 MHz, $CDCl_3$): δ 4.89 (s, 2H, C_5H_4), 4.56 (m, 2H, Fc-CH_2), 4.35 (s, 2H, C_5H_4), 4.33 (s, 5H, C_5H_5), 3.36 (m, 2H, NCH_2), 3.23 (s, 6H, $N(CH_3)_2$), 1.84 (m, 2H, $CH_2CH_2CH_3$), 1.04 (t, 3H, J = 7.3 Hz, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$): δ 72.22 (C_5H_4), 72.07 (C_5H_4), 70.62 (C_5H_4), 69.67 (C_5H_5), 65.57 ($C_5H_4CH_2$), 64.73 (NCH_2), 49.99 (NCH_3), 16.50 (CH_2CH_3), 10.68 (CH_3).

*2.2.1.2. Data for (ferrocenylmethyl)butyldimethylammonium nitrate (**2**).* Yellow powder, Yield: 1.45 g (80.2%). m.p:136.1–138.0 °C. *Anal.* Found: C, 56.17; H, 7.38; N, 7.45. Calcd.: C, 56.37; H, 7.23; N, 7.73%. IR(KBr): cm^{-1}, 3095m, 3024w, 2960m, 2860m, 1585m, 1481m, 1371s, 1344vs, 1246m, 1109m, 1043m, 997m, 838s, 705m. ^1H NMR (400 MHz, $CDCl_3$): δ 4.61 (s, 2H, C_5H_4), 4.45 (m, 2H, Fc-CH_2), 4.35 (t, 2H, C_5H_4), 4.27 (s, 5H, C_5H_5), 3.21 (m, 2H, NCH_2), 3.08 (s, 6H, $N(CH_3)_2$), 1.80 (m, 2H, $CH_2CH_2CH_3$), 1.02