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Evaluation of Ferrocene Derivatives as Burn Rate Modifiers in AP/HTPB-Based Composite Propellants

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ABSTRACT

Some ferrocene derivatives like 2,4-dinitrophenylhydrazine derivative of acetyl ferrocene, 1-pyrrolidinylmethyl ferrocene, di-ter-butyl ferrocene and 1,3-diferrocenyl-1-butene (DFB) have been synthesised and characterised by infrared, nuclear magnetic resonance, ultraviolet, iron content, etc. To study the effect of their incorporation on performance, ammonium perchlorate/hydroxyl-terminated polybutadiene-based composite propellants containing these derivatives have been prepared and studied for burn rates, tensile strength and percentage elongation followed by their static test evaluation. A comparison of the properties of propellant containing solid and liquid ferrocene derivatives has been made with those containing Fe_2O_3 and *n*-butyl ferrocene, respectively. The data clearly indicates that these ferrocene derivatives are better than Fe_2O_3 and *n*-butyl ferrocene. Also, DFB is the best among these derivatives. Like composite propellants, DFB increases burn rate in fuel-rich propellants also.

1. INTRODUCTION

Composite propellants are used for military and space applications. Ammonium perchlorate (AP)-based formulations of composite propellants consist of Fe_2O_3 or $CuCr_2O_4$ as burn rate catalysts. Some European and American countries have recently reported the use of ferrocene derivatives in place of Fe_2O_3 or $CuCr_2O_4$ in these propellants[1-10]. Ferrocene derivatives impart high burn rates to these propellants. Further, some ferrocene derivatives have also been reported as crosslinking agents and plasticisers, in addition to burn rate accelerators. However, the use of ferrocene derivatives create some problems like their migration from propellants to surface, oxidation during storage, etc. To obviate these problems, SNPE, France, has developed a butacene binder, hydroxyl-terminated polybutadiene (HTPB) which chemically reacts with a ferrocene derivative. Most of the information in this area is either patented or is available in the form of classified reports. It was therefore considered of interest to synthesise and characterise some ferrocene derivatives which do not have these shortcomings and to evaluate their performance in composite propellants. For this purpose, a number of ferrocene derivatives have been reported.

Based on the ease of synthesis, yield, purity, etc., four ferrocene derivatives, viz., 2,4-dinitrophenylhydrazine derivative of acetyl ferrocene, 1-pyrrolidinyl methyl ferrocene, di-ter-butyl ferrocene and 1,3-diferrocenyl-1-butene (DFB) have been selected, synthesised and characterised by infrared (IR), and nuclear magnetic resonance (NMR), and for iron content (Table 1).

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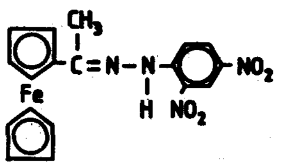
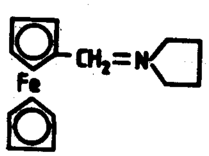
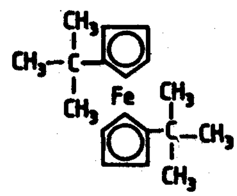
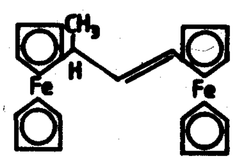
Table 1. IR and ^{1}H-NMR data and structures for ferrocene derivatives

	2,4-Dinitrophenylhydrazine derivative of acetyl ferrocene	1-Pyrrolidinyl methyl ferrocene	Di-ter-butyl ferrocene	1,3-Diferrocenyl-1-butene
* Iron (%)	14.0	28.0	19.0	25.5
IR peaks (cm^{-1})	1100, 995 (Ferrocenyl group) Carbonyl group absent 3300 (-NH group) 1520 (-NO_2 group)	1100, 1000, 3095 (Ferrocenyl group)	Peaks at 1100 and 995 for ferrocene group are absent because it is disubstituted.	(3090, 1102, 1000) (Ferrocenyl group) (2966, 2864, 1465) (Methyl group) (3090, 1300, 962) Vinyl group 1638-Double bond
NMR	2,4 δ Corres. to ($3H$, s) 4,10 δ Corres. to (5H, s) 4, 28 δ Corres. to ($2H$, s) 4,58 δ Corres. to ($2H$, s) 7.2 – 7.9 δ Benzene ($3H$) 10.2 δ Corres. to $1H$	1,8 δ Corres. to ($4H$, s) 2,4 δ Corres. to ($4H$, s) 3.32 δ Corres. to ($2H$, s) 4.00 δ Corres. to ($9H$ s)	1.2 δ Corres. to (18 H) Singlet methyl group Ferrocenyl protons 1.4 δ 8 H Singlet	Vinyl proton 6 δ ($2H$) Complex ferrocenyl Proton and methine proton 4.4 - 3.9 δ ($19H$) Complex methyl proton 1.88 δ ($3H$) doublet
Structures				

* Experimental results

These compounds have also been evaluated for their performance in composite propellants.

2. EXPERIMENTAL PROCEDURE

2.1 Materials

The raw materials used for synthesis were: (i) main starting material, ferrocene was of Sigma/Aldrich/Merck make with purity of 97-98 per cent, and (ii) other chemicals like acetic anhydride, orthophosphoric acid, formaldehyde, diethyl ether, ethyl alcohol, hydrochloric acid , dimethyl amine, pyrrolidine, sodium hydroxide, aluminium chloride, etc. were of L.R. grade.

2.2 Synthesis

Synthesis of 2,4-dinitrophenylhydrazine derivative of acetyl ferrocene[1], 1-pyrrolidinyl methyl ferrocene[2], di-ter-butyl ferrocene[3] and DFB[4] was carried out by already developed methods. The structures of these derivatives along with their IR and NMR data are shown in Table 1.

2.3 Analysis

(a) Infrared spectrophotometer (Perkin-Elmer Model-683) and FTIR (Perkin-Elmer Model-1605) were used for recording IR/FTIR spectra. IR spectra of solid and liquid derivatives were recorded by *KBr*/Nujol and smear methods, respectively.

(b) Ultraviolet spectra were recorded on ultraviolet-visible-NIR spectrophotometer (Hitachi Model-340-C).

(c) Differential thermal analyser thermograms were recorded on locally-fabricated micro-DTA.

(d) Viscosity was measured using digital Brookfield viscometer.

(e) ^1H-NMR spectra were recorded with Bruker 90 MHz FT NMR using $CdCl_3$ as a solvent with tetramethyl silane (TMS) as an internal standard.

Thin layer chromatography (TLC) on silica gel was used to monitor reaction and identify the final compounds. Column chromatography technique was used to get compounds of required purity.

2.4 Propellants Casting & Evaluation

The propellants used were mainly of the following composition:

(a) Solid loading (85 %) containing bimodal AP [mixture of AP(coarse)-250μ and AP(fine)-8-10μ], aluminium powder and Fe_2O_3 or ferrocene derivative (if solid).

(b) Binder (15 %) containing HTPB, dioctyl adipate, toluene diisocyanate, pyrogallol, MAT [an adduct of MAPO (tris-methylazeridinyl phosphine oxide), adipic acid and tartaric acid] and lecithin were cast.

The above composition in batch size of 6/12 kg was processed and cast. The propellant grain of dimensions (ID-60 mm, OD-115 mm, length–200 mm and weight–2.5 kg were cut and evaluated statically in ballistic evaluation motor (BEM). Throat diameter of either 23 or 28 mm was used. The propellant grains were fired in regressive mode after conditioning loaded motors for 24 hr at the required temperature. Some dumbbells were also made to determine their mechanical properties. Propellant pieces and powder sample were used to determine density and cal-val, respectively.

3. RESULTS & DISCUSSION

The iron content, ^1H-NMR and IR frequencies along with their assignments for 2,4-dinitrophenyl hydrazine derivative of acetyl ferrocene, 1-pyrrolidinyl methyl ferrocene, di-ter-butyl ferrocene and DFB are given in Table 1. This indicates that these derivatives conform to the reported structures.

Before incorporating these ferrocene derivatives in propellant compositions, some additional tests like acidity, p*H*, water content, solubility in HTPB/DOA, and decomposition temperatures (in air/nitrogen) were also carried out (Table 2). The

Table 2. Some physical properties of ferrocene derivatives

Compound	Density (g/cc)	Solubility in *DOA at 40 °C (g/ml)	Iron content (%)	Melting point/boiling point (°C)	Acidity content (p*H*)	Water content (%)
2,4-Dinitrophenylhydrazine derivative of acetyl ferrocene	1.62	1.2	13.7	217 Decomposition	7	Nil
1, Pyrrolidinyl methyl ferrocene	1.22	6.0	20.7	50 No decomposition, only sublimation	10	0.03
Di-ter-butyl ferrocene	1.12	-	18.7	BP range 110-120 at 0.6 mm	7	Nil
1,3-Diferrocenyl-1-butene	1.32	-	26.5	340-380 Decomposition	7	0.05

* DOA - diocetyl adipate: plasticiser, component of binder

Table 3. Burn rate and other properties of composite propellant formulations containing different ferrocene derivatives and ferric oxide

Ingrediants\results		Composite propellant formulation numbers									
		1	2	3	4	5	6	7	8	9	10
Ammonium perchlorate 250 µ (%)		33.5	33.5	33.5	33.5	33.5	34.0	33.5	33.5	8	8
Ammonium perchlorate 8-10 µ (%)		33.5	33.5	33.5	33.5	33.5	34.0	-	-	-	-
Ammonium perchlorate 4 µ (%)		-	-	-	-	-	-	33.5	33.5	72	72
Aluminium (%)		17	17	17	17	17	17	17	17	-	-
Binder (%)		15	15	15	15	15	15	15	15	20	20
Iron oxide (%)		1	-	-	-	-	-	-	-	-	-
2,4-Di-nitrophenylhydrazine derivative of monoacetyl ferrocene		-	1	-	-	-	-	-	-	-	-
1-Pyrrolidinyl methyl ferrocene		-	-	1	-	-	-	-	-	-	-
Di-ter-butyl ferrocene		-	-	-	1	-	-	-	-	-	-
1,3-Diferrocenyl-1-butene		-	-	-	-	1	2	2	-	2	-
n-Butyl ferrocene		-	-	-	-	-	-	-	2	-	2
Tensile strength (kg/cm^2)		10	13	12.6	10	10	11	7.5	8	7	7.2
Percentage elongation		10	10	8	12	17	17	13	12	22	22
* Burn rate (mm/s) 70 KSC		9.5	10	12	9.5	9.8	12	12.1	11.8	34	32
Cal-val (cal/g)		1412	1488	1410	1408	1400	1406	1330	1330	967	960
Density (g/ml)		1.72	1.74	1.74	1.74	1.74	1.74	1.73	1.72	1.62	1.62
**Ballistic parameters	Pressure range KSC	-	-	70-90	66-72	62-73	80-121	-	-	-	-
	Pressure average KSC	-	-	77	66	85	93	-	-	-	-
	Burn rate (mm/s) 70 KSC	-	-	11.5	9.5	9.8	11.5	-	-	-	-

* Strand burner results, ** BEM firing results

burn rate data of composite propellants containing different ferrocene derivatives are shown in Table 3.

3.1 2,4-Dinitrophenylhydrazine Derivative of Acetyl Ferrocene (Solid)

Table 3 shows that the propellant containing this derivative (formulations 1 & 2) gives burn rate of 10 mm/s at 70 KSC which is comparable to that of Fe_2O_3 containing propellant. In addition, it improves cal-val and tensile strength (TS) and also does not adversely affect processing of propellant slurry at the time of casting. Hence, it is concluded that this derivative is as good as Fe_2O_3, but at the same time, it improves TS.

3.2 1-Pyrrolidinyl Methyl Ferrocene (Solid)

This derivative gives the burn rate of 12 mm/s at 70 KSC which is 20 per cent more than that of Fe_2O_3 containing propellant (formulation 3). In addition, it improves TS but reduces percentage elongation. It also does not adversely affect processing of propellant mix at the time of casting of propellant. Hence, this derivative is better than Fe_2O_3 and improves TS also.

3.3 Di-Ter-Butyl Ferrocene (Liquid)

This derivative gives the burn rate of 9.5 mm/s at 70 KSC (formulation 4) which is comparable to that of Fe_2O_3 containing propellant. It also slightly improves percentage elongation. It is observed that the curing of the propellant with toluene diisocyanate (component of binder) as a curing agent is accelerated by this compound and as a result, pot life of the propellant is reduced.

The tubular propellant grains containing 1-pyrrolidinyl methyl ferrocene and di-ter-butyl ferrocene were fired statically in BEM. Smooth pressure-time profiles were obtained. Ballistic parameters are shown in Table 3.

3.4 1,3-Diferrocenyl-1-Butene (Liquid)

The performance of the propellant is compared with Fe_2O_3 as well as *n*-butyl ferrocene (liquid). The formulations with the incorporation of DFB were made and cast in tray to study compatibility of this derivative with other ingredients and also its curing pattern. It is observed that this derivative accelerated curing if toluene diisocyanate is used as a curing agent and thus reduces the pot life of propellant mix. However, in the absence of curing catalyst like ferric acetylacetonate, adequate pot life is obtained. So, further castings were done by eliminating ferric acetylacetonate in propellant compositions.

The data shows that this derivative gives the burn rate of 9.8 mm/s at 70 KSC (formulation 5), which is comparable with that of Fe_2O_3 containing propellant. Further, it improves percentage elongation which indicates that it acts as a plasticiser also.

The effect of concentration of this ferrocene derivative on burn rate and other properties is also given in Table 3 (formulations 5 and 6). The data indicate that the burn rate increased by 2 mm/s and elongation has also increased by 17 per cent as compared to that of Fe_2O_3 containing propellants.

Table 4. Data on non-aluminised composite propellant containing 1,3-diferrocenyl-1-butene and *n*-butyl ferrocene at different temperatures

Propellant composition of ammonium perchlorate		
AP coarse/fine (35:65)	- 80 %	
AP fine (4μ)	-	
Binder	- 20 %	
Catalyst	- 2 parts	
Mechanical properties		
Catalyst	1,3-Diferrocenyl -1-butene (DFB)	*n*-Butyl ferrocene
TS (kg/cm^2)	4.6	4.4
Percentage elongation	18-22	15-20
Ballistic evaluation motor firing results		
Catalyst	1,3-Diferrocenyl-1-butene	*n*-Butyl ferrocene
Temperature (°C)	Pressure range (kg/cm^2)	Pressure range (kg/cm^2)
- 30	73-87	-
+ 31	90-104	85-100
+ 55	100-109	93-105
	Pressure average (kg/cm^2)	Pressure average (kg/cm^2)
- 30	78	71
+ 31	97	91
+ 55	105	96
	Burn rate (mm/s)	Burn rate (mm/s)
- 30 at 75 kg/cm^2	20.0	17.0
+ 31 at 90 kg/cm^2	27.8	25.0
+ 55 at 100 kg/cm^2	29.0	27.0

Tubular propellant grains containing one and two per cent DFB were fired statically in BEM. A smooth pressure-time profile was obtained. Based on this data, it is concluded that this compound is as good as Fe_2O_3 and at the same time, it also acts as a plasticiser.

The effect of DFB has also been compared with that of *n*-butyl ferrocene on the burn rate of propellant (formulations 7 and 8). It is seen that burn rate is 12.1 mm/s and elongation is 13 per cent for DFB containing propellant as against 11.8 mm/s and 12 per cent, respectively for *n*-butyl ferrocene containing propellant. Similar observation is also recorded for another propellant formulation, where burn rate with the use of DFB is 34 mm/s as against 32 mm/s in case of *n*-butyl ferrocene (formulations 9 and 10).

The efficiency of DFB containing propellant was studied over a wide range of temperatures using 15 kg batch of propellant formulation. Tubular propellant grains containing DFB and *n*-butyl ferrocene were static-tested in BEM in regressive mode. Smooth pressure-time profiles were obtained. The results are given in Table 4. It is evident that burn rates of DFB containing propellants are higher at all temperatures as compared to that of *n*-butyl ferrocene.

The efficacy of DFB in fuel-rich formulation has also been studied and the data on static evaluation of fuel-rich propellant is shown in Table 5. It is clear that DFB enhances the burn rate of fuel-rich propellants also, similar to *n*-butyl ferrocene in composite propellants.

Table 5. Burn rate of fuel-rich composite propellants with 1,3-diferrocenyl-1-butene and *n*-butyl ferrocene

Propellant composition		Catalyst	Burn rate (mm/s) at 50 (kg/cm^2)
AP	- 45 %		
Binder (HTPB)	- 35 %	1,3-Diferrocenyl-	
Polystyrene	- 15 %	1-butene (DFB)	2.4
Magnesium	- 5 %	n-Butyl ferrocene	2.4
Catalyst	- 1 part		

4. CONCLUSIONS

All ferrocene derivatives used in this study increase the burn rate of AP/HTPB-based propellants. 2,4-Dinitrophenylhydrazine derivative of acetyl ferrocene,. 1-pyrrolidinyl methyl ferrocene, di-ter-butyl ferrocene and DFB are as effective as Fe_2O_3 for improving burn rates. However, DFB being liquid, has an edge over Fe_2O_3 and facilitates increase in solid loading. It also improves mechanical properties and increases burn rates as compared to *n*-butyl ferrocene in composite propellants as well as fuel-rich propellants.

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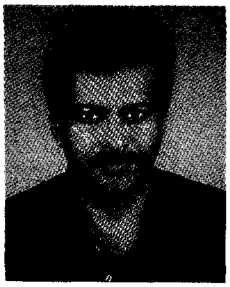

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