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Evaluation of various dihydric and trihydric phenols as stabilizers for composite modified double base (CMDB) propellants

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Abstract

This paper reports thermal analysis results of the various di- and trihydric phenols containing composite modified double base (CMDB) propellants. Thermal stability test results revealed higher stability of phloroglucinol based CMDB propellants than catechol, hydroquinone and pyrogallol based compositions. The activation energy (E_a) as computed from isothermal gravimetric analysis (120–140°C) comes to 29.8 kcal/mol for phloroglucinol based CMDB composition, which is comparable to E_a for resorcinol containing composition but higher than that for catechol, hydroquinone and pyrogallol (18–20 kcal/mol) based compositions. Autoignition test results also gave a similar trend for activation energies. A shelf lifetime of 57 years was obtained for the phloroglucinol based composition, which is marginally lower than that for the resorcinol containing composition (73 y). Shelf lifetime (the time up to which a propellant can be stored without hazards) for catechol, hydroquinone and pyrogallol containing compositions was computed to be 1–1.5 y. In general, *meta*-substituted polyhydroxy benzenes are superior stabilizers than *ortho*- and *para*-substituted ones.

Introduction

Composite modified double base (CMDB) propellants of higher energy and superior mechanical properties are prefered for propulsion of military and space vehicles [1]. However, CMDB propellants containing ammonium perchlorate (AP) dispersed in a double base (DB) matrix are reported to have lower shelf life due to strongly autocatalytic decomposition reactions that occur during ageing. It has also been reported that the shelf life of AP-based CMDB propellant is lower than that of cyclotrimethylene trinitramine (RDX)- and pentaerythritol tetranitrate (PETN)-based CMDB compositions [2]. To overcome the ageing problem of AP-based CMDB propellants generally, stabilizers like resorcinol, alkoxy-phenoxy benzenes, metal oxides or combination of *p*-nitro-*N*-methyl-aniline (PNMA) with aluminium silicates are reported to be incorporated in the composition [3–6]. We have reported earlier that resorcinol has superior stabilization effect than its derivatives, metal oxides and PNMA [7]. 2-Nitrodiphenylamine (NDPA) and carbamite, which are com-

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monly used as stabilizer, are not effective in the CMDB system, however, it is reported that resorcinol incorporated even in combination with these stabilizers offers sufficiently stable AP-based CMDB propellants [7,8]. A number of researchers have suggested that AP catalyzes the autodecomposition of DBP through the involvement of its oxygen-rich decomposition product namely perchloric acid ($HClO_4$) [8–9].

Hartman and Musso [10] have explained the effectiveness of resorcinol due to activated aromatic ring formation, which helps in absorption of nitrogen oxides quickly and more effectively, resulting in further control of growth of autocatalytic reactions.

The present study was undertaken to find out whether dihydric and trihydric phenols (catechol, hydroquinone and pyrogallol, phloroglucinol) can be used as effective stabilizer in place of resorcinol and to get more insight on the mechanism of stabilization of CMDB propellants. Thermal tests, namely the Abel heat test, the methyl violet test, the vacuum stability test, differential thermal analysis (DTA), gas kinetics, isothermal gravimetric analysis (IGA) and time to autoignition were used for comparative evaluation.

Experimental

Propellant samples were prepared by slurry cast technique [11], incorporating 30% spheroidal nitrocellulose (SNC), 28% nitroglycerin (NG), 7% Diethylphthalate and 35% AP. The spheroidal nitrocellulose was comprised of 88.9% NC (12.2% N content), 7.1% NG, 1.4% dibutylphthalate (DBP) and 2.6% carbamite. Dihydric and trihydric phenols of 98% purity procured from the trade were incorporated in 2 parts over the composition.

The Abel heat test (64.5°C), methyl violet (MV) test (120°C) and vacuum stability (VS) test (90°C) as described elsewhere for DBP [12] were applied. In view of strong autocatalytic behaviour of CMDB propellants, the VS test was modified to lower sample weight (2.5 g).

For thermal analysis a DTA instrument of 'NETZSCH' make was used to study the decomposition behaviour. All experiments were carried out under atmospheric conditions. Isothermal gravimetric analysis (IGA) was carried out at 120 and 140°C in an incubator with temperature control accuracy of ± 0.5°C. Samples of 200 mg were used.

Time to autoignition test as described by Rice et al. [8] was applied to assess the shelf lifetime of CMDB compositions. Rice and coworkers [8] have established correlation between resorcinol content and time to autoignition for AP-based CMDB propellants. Details regarding instrumentation as well as methodology used and the precision of lifetime estimates are given in our earlier publications [2,13].

Results and discussion

The effectiveness of dihydric and trihydric phenols as compared to resorcinol as stabilizer for CMDB propellants was evaluated in the first phase of study. Stability test results as given in Table 1 bring out lower stability of the catechol and hydroquinone based compositions than the resorcinol containing formulation.

Results of gas kinetic and IGA studies showed a similar pattern (Table 2). The activation energy, E_a, computed from IGA for catechol and hydroquinone was lower than that for resorcinol based compositions by 10 kcal/mol.

Thermal analysis (DTA) results (Table 3) revealed lower peak-decomposition temperatures (T_m) for catechol and hydroquinone based compositions (163°C) than for resorcinol stabilized propellant (182°C).

These findings suggest that catechol and hydroquinone have poor stabilization potential and behave more or less like resorcinol mono- and diacetates as reported in our previous study [7].

Time to autoignition (Table 4) at 140°C for catechol and hydroquinone stabilized compositions was found to be almost half of that of resorcinol containing compositions. The latter recorded relatively higher values at 150 and 160°C also. The Arrhenius plot of data so obtained (see Fig. 1) gave an E_a value of about 23 kcal/mol for formulations containing catechol and hydroquinone, while E_a for resorcinol based composition was 31 kcal/mol. From

TABLE 1

Results of stability tests for CMDB propellants containing dihydric and trihydric phenols

Stabilizer (2 parts)	Abel heat test at 64.5°C (min)	Methyl violet test at 120°C (min)		Vacuum stability test at 90°C (volume of gases evolved in ml)
Resorcinol	20	a. Color change	85	
		b. No brown fumes		0.8
		c. No explosion		
Catechol	14	a. Color change	35	
		b. Brown fumes	155	1.4
		c. Explosion	160	
Hydroquinone	12	a. Color change	25	
		b. Brown fumes	45	5
		c. Explosion	60	
Pyrogallol	8	a. Color change	25	
		b. Brown fumes	65	5.3
		c. Explosion	70	
Phloroglucinol	20	a. Color change	85	
		b. No brown fumes		0.7
		c. No explosion		

TABLE 2

Results of gas kinetics and isothermal gravimetric analysis of CMDB propellants containing dihydric and trihydric phenols

Stabilizer (2 parts)	Gas Kinetics			Isothermal gravimetric analysis		
	Volume of gases evolved (ml) at different intervals of time at 100 °C			Time (min) required for 5% weight loss		Activation energy (kcal/mol)
	4 h	8 h	12 h	120 °C	140 °C	
Resorcinol	0.1	0.2	0.4	137	21	30
Catechol	0.4	0.7	1	58	17	20
Hydroquinone	0.9	2	3	60	17	20
Pyrogallol	0.6	1.3	2	50	16	18
Phloroglucinol	0.1	0.4	0.6	127	20	29.8

TABLE 3

DTA results for CMDB propellants containing dihydric and trihydric phenols

Stabilizer (2 parts)	Decomposition temperatures (°C)[a]		
	T_i	T_m	T_f
Resorcinol	179	182	193
Catechol	132	163	187
Hydroquinone	138	163	187
Pyrogallol	146	155	185
Phloroglucinol	150	170	193

[a] T_i is inception, and T_f in final temperature.

TABLE 4

Results of time to autoignition test of CMDB propellants containing dihydric and trihydric phenols

Stabilizer (2 parts)	Time to autoignition (min)			Activation energy (kcal/mol)	Lifetime at 30 °C (y)
	140 °C	150 °C	160 °C		
Resorcinol	39.8	18.6	7.9	30.9	73
Catechol	21	12	6	22.4	1
Hydroquinone	24	13.4	7	23.2	1.5
Pyrogallol	20	11.5	6	22	1
Phloroglucinol	36	17	6.7	30.5	57

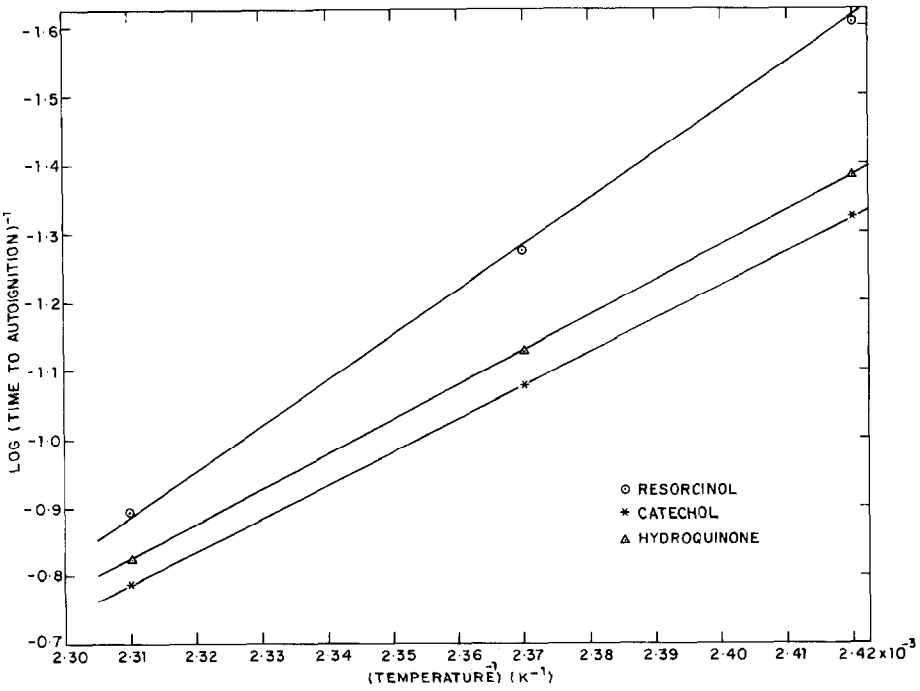

Fig. 1. Arrhenius plot of autoignition test results for resorcinol, catechol and hydroquinone.

these results a shelf lifetime of about 1–1.5 y was calculated for formulations containing catechol and hydroquinone. For the resorcinol stabilized composition, a lifetime of 73 y was calculated.

In the second phase of study, the effect of trihydric phenols (namely, pyrogallol and phloroglucinol) was evaluated. Stability test results indicate that phloroglucinol is close to resorcinol in its effectiveness as stabilizer for the AP-based CMDB composition. However, the pyrogallol containing composition appears to have lower stability. Gas kinetics and IGA results revealed a similar trend (Table 2). In DTA, for the phloroglucinol based composition a higher T_m than for pyrogallol based composition was recorded (Table 3).

The time to autoignition test results also established superiority of phloroglucinol to pyrogallol as stabilizer (Table 4). For phloroglucinol and pyrogallol containing compositions E_a values of 30.5 and 22 kcal/mol were computed, respectively. A shelf lifetime of 57 y was obtained for phloroglucinol containing CMDB propellant from these results. For the pyrogallol incorporated composition the lifetime works out to be merely 1 y (Fig. 2).

These results establish that phloroglucinol is a superior stabilizer than MgO, Co_2O_3 and PNMA which were evaluated in our previous studies [7].

The present findings bring out that polyhydric phenols having hydroxyl groups *meta*-positioned to each other (resorcinol and phloroglucinol) are su-

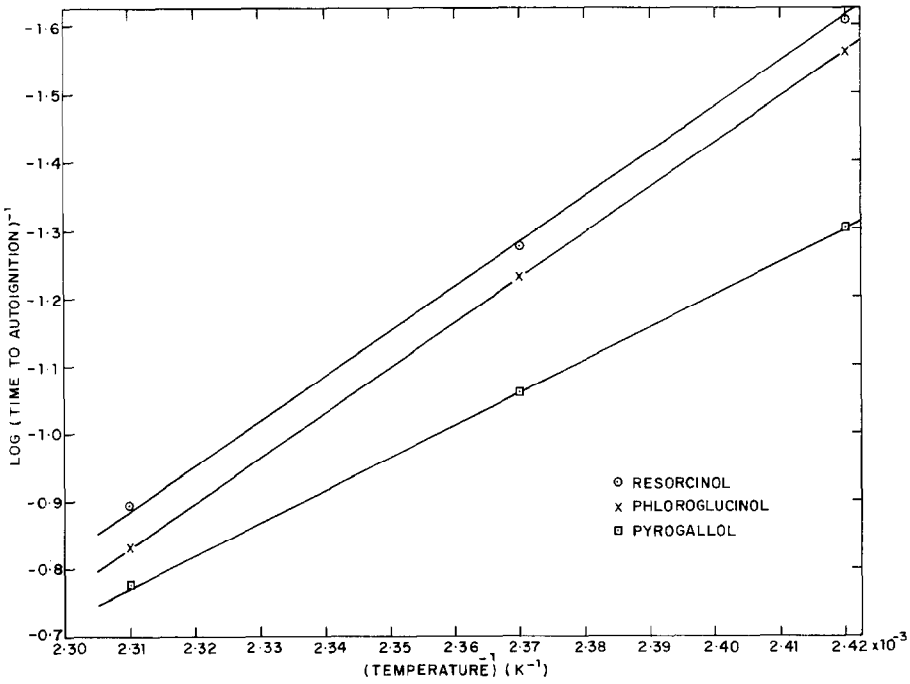

Fig. 2. Arrhenius plot of autoignition test results for resorcinol, phloroglucinol and pyrogallol.

perior stabilizers for CMDB propellants as compared to polyhydric phenols having hydroxy groups *ortho*-(catechol, pyrogallol) and *para*-positioned (hydroquinone) to each other. This behaviour of polyhydric phenols can be explained on the basis of the fact that polyhydric phenols with *ortho*- or *para*-hydroxy groups are more susceptible to oxidation by the generated $HClO_4$ from AP, in view of the possibility of the formation of conjugated cyclic oxidation products, the so-called quinones [14]. A similar process may be operative in the case of pyrogallol also. On the other hand, meta-substituted polyhydric phenols do not undergo such oxidation reactions easily as they cannot form cyclic conjugated quinones.

The lower stability of the phloroglucinol-based CMDB propellant as compared to the resorcinol containing composition may be due to the reason that its keto-form is energetically nearer to the trienolic form, thereby reducing the effective concentration of the enolic form with electron rich aromatic ring. Further, in the mono-keto form of phloroglucinol remaining hydroxyl groups are strongly acidic due to their conjugation with the carbonyl group through one or two ethylenic double bond [14].

Conclusions

(1) Phloroglucinol is a more superior stabilizer for CMDB systems than pyrogallol, catechol and hydroquinone. However, it is less effective than resorcinol.

(2) Lower effectiveness of catechol, hydroquinone and pyrogallol may be due to their rapid oxidation to conjugated cyclic quinones.

(3) The shelf lifetime of phloroglucinol containing CMDB propellants is expected to be 57 y.

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