

不同粘合剂 RDX/AP 推进剂 燃烧产物的分析研究*

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摘要: 以聚醚、HTPB、NEPE 三种不同粘合剂体系的 RDX/AP 少烟推进剂为研究对象, 用裂解色谱-质谱联用技术分析它们的裂解产物的组成。发现推进剂中所采用的粘合剂类型不同时, 其裂解产物的组成和含量不同, NEPE 少烟推进剂基峰44占70%, 聚醚少烟推进剂基峰44只占10%, 这是造成两类推进剂压强指数不同的原因。

主题词: 固体推进剂, 燃烧产物, 仪器分析

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COMBUSTION PRODUCTS ANALYSIS OF RDX/AP PROPELLANT WITH DIFFERENT BINDERS

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Abstract: Smoke reduced propellants with different binders such as HTPB, Polyether, NEPE are studied. The composition of the pyrolytic products are measured by PYGC-MS. The result shows that the products and their contents in pyrolytic processes are different. The measured value representing the 44 peak in the NEPE smoke-reduced propellant is 70% of the total value, while the one in the polyether smoke-reduced propellant is only 10%, which results in the difference in pressure exponent between these two propellants.

Subject terms: Solid propellant, Combustion product, Instrumental analysis

1 引言

固体推进剂燃烧领域的研究仍有许多悬而未决的难题和新的应用研究有待开发, 本文利用较先进的裂解色谱-质谱联用仪分析固体推进剂的燃烧气体的组成、瞬间的化学变化, 了解其粘合剂种类的差异导致燃烧性能发生的变化, 比热物理法和数学模型深刻得多, 解决它更有的放矢。

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2 实验方法

用聚醚、HTPB、NEPE 三种粘合剂制成含有40%RDX 的低铝推进剂,在由裂解进样器、HP5890气相色谱仪和 HP5971质谱仪三部分组成的仪器上进行分析(称 PYGC-MC 联用技术)。裂解器裂解温度控制在600℃、裂解10s,进样器温度为250℃,气相色谱仪采用0.22mm 的石英毛细管柱和 SE-54固定液。实验时先控制柱温在50℃下5min,然后以10℃/min 的速率升温到250℃、保持5min,质谱仪检测器温度控制在180℃,测定三种推进剂燃速、压强指数。

3 实验结果^[1]

(1) 三种推进剂燃速、压强指数见表1。由表1可见三种推进剂压强指数截然不同,与燃烧产物的组成密切相关。

(2) 三种推进剂的裂解产物的组成见表2~4。

Table 1 Result of combustion performance

Propellant type	$r_{2.9\text{MPa}}/$ (mm/s)	$r_{8.83\text{MPa}}/$ (mm/s)	n (2.94—8.83MPa)	$\Delta r/\%$
Polyether propellant	5.07	7.68	0.41	51
HTPB propellant	4.47	7.21	0.44	61
Minor-smoke propellant	5.73	10.83	0.58	89

Table 2 The main component of the polyether propellant pyrolytic products

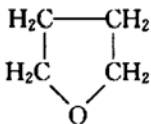
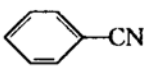
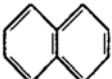
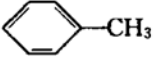
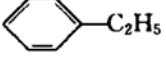
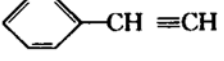
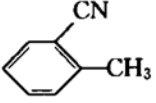
Order	Reining time (ms)	Basic peak mass number	Pyrolytic products structure	Peak area (%)	Memo
1	1.60	44	CO ₂ , N ₂ O	10.47	Guesswork
2	1.73	44	CH ₃ CHO	17.36	Guesswork
3	1.88	58	CH ₃ CH ₂ CHO	2.01	Guesswork
4	2.12	70	Cl ₂	3.66	Guesswork
5	2.61	72		35.95	Appraisal
6	2.93	78		8.60	Appraisal
7	10.87	103		3.56	Appraisal
8	14.98	128		2.00	Appraisal

Table 2 Continued

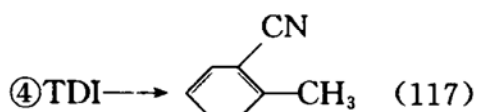
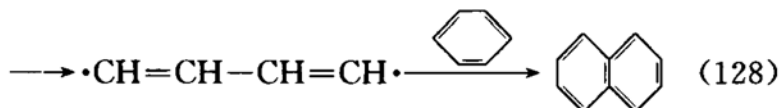
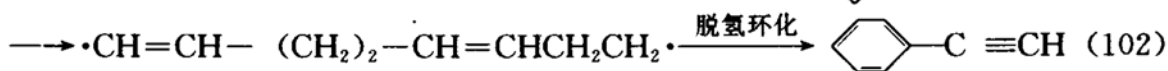
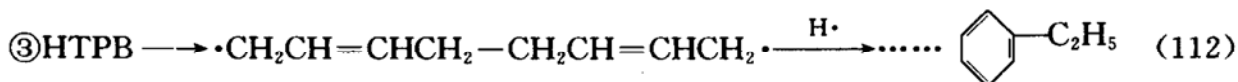
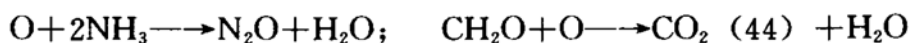
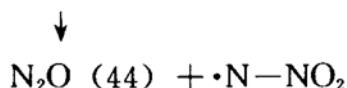
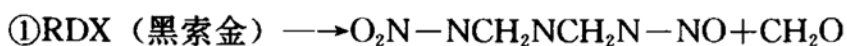
Order	Reining time (ms)	Basic peak mass number	Pyrolytic products structure	Peak area (%)	Memo
9	15.55	112	$(\text{CH}_3)_2\text{CH}(\text{CH}_2)_3\text{CH}=\text{CH}_2$	1.75	Guesswork
10	22.16	142	$\text{CH}_3(\text{CH}_2)_7\text{CHO}$	2.05	Guesswork
11	24.71	270	$\text{CH}_3(\text{CH}_2)_{14}\text{COOCH}_3$	3.10	Appraisal
12	27.02	298	$\text{CH}_3(\text{CH}_2)_{16}\text{COOCH}_3$	5.79	Appraisal

Table 3 The main component of the HTPB propellant pyrolytic products

Order	Reining time (ms)	Basic peak mass number	Pyrolytic products structure	Memo
1	1.61	44	$\text{CO}_2, \text{N}_2\text{O}$	Guesswork
2	2.16	46	HCOOH	Guesswork
3	2.27	84	HClO_3	Guesswork
4	2.91	78		Appraisal
5	4.81	92		Appraisal
6	5.41	112		Guesswork
7	8.04	102		Guesswork
8	12.19	117		Guesswork
9	14.92	128		Appraisal
10	20.92	128	$(\text{CH}_3)_2\text{CH}(\text{CH}_2)_4\text{CHO}$	Guesswork
11	22.14	142	$\text{CH}_3(\text{CH}_2)_7\text{CHO}$	Guesswork
12	24.69	270	$\text{CH}_3(\text{CH}_2)_{14}\text{COOCH}_3$	Appraisal
13	26.99	298	$\text{CH}_3(\text{CH}_2)_{16}\text{COOCH}_3$	Appraisal

* Not get out peak area in computer.

主要组成是 RDX、AP、聚醚或 HTPB 的推进剂, 上述产物形成的过程可能是:



还有增塑剂、防老剂、工艺助剂的裂解产物。

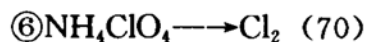
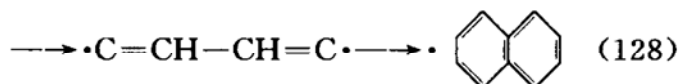
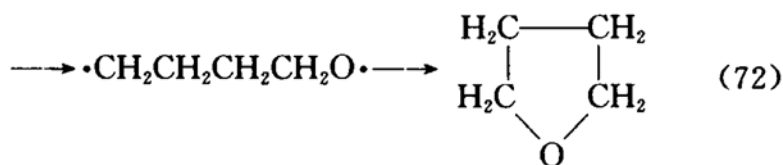
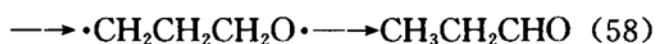
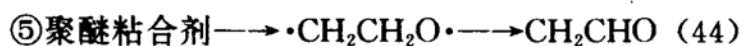
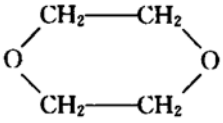
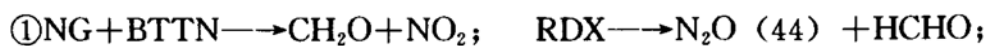


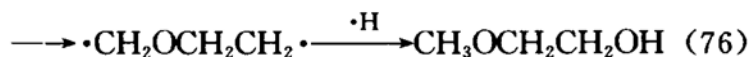
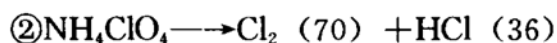
Table 4 The main component of the NEPE minor-smoke propellant pyrolytic products

Order	Reining time (ms)	Basic peak mass number	Pyrolytic products structure	Peak area (%)	Memo
1	1.62	44	$\text{N}_2\text{O}, \text{CO}_2$	72.34	Guesswork
2	2.10	70	Cl_2	6.06	Guesswork
3	2.30	36	HCl	0.97	Guesswork
4	2.33	46	HCOOH	4.99	Guesswork
5	2.43	74	$\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$	3.09	Guesswork
6	3.56	88		3.81	Guesswork
7	9.33	89	$\text{CH}_3\text{CH}_2\text{NHCOOH}$	0.91	Guesswork
8	17.58	76	$\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH}$	0.45	Guesswork

NEPE 主要组成是 RDX, NG+BTTN, AP, PEG 等。上述产物形成过程可能是:



$\text{NO}_2 + \text{HCHO} \longrightarrow \text{N}_2\text{O} (44) + \text{CO}_2 (44)$ 。为推进剂主要裂解产物。



从裂解产物分析,常压600°C时,HTPB的裂解产物主要是 N_2O , CO_2 以及苯等;聚醚推进剂的主要裂解产物是 N_2O , CO_2 和THF;NEPE推进剂裂解产物绝大部分是 N_2O 和 CO_2 ,三种推进剂均未发现 NO_2 的存在。原因可能是:有人发现温度高于750°C其裂解产物中主要是氮氧化物,如NO,而不是 NO_2 ;其二是起始阶段,从 $-\text{O}-\text{NO}_2$ 键断裂开始,生成的 NO_2 与HCHO反应也发生在起始阶段, NO_2 在反应区内寿命很短,另外在凝聚相内的 NO_2 已与HCHO开始反应,所以在表面上已几乎反应完生成CO和NO。第二种说法比较吻合本实验结果。

4 结果讨论^[2,3]

三种粘合剂为基的少烟推进剂,其聚醚和HTPB粘合剂主骨架以CH为主,前者骨架中含有柔性较好的醚键,本身流动性好、易熔、热解温度低,随压强的提高更容易使熔融的粘合剂覆盖其燃面,而造成局部熄火,使较高压强内的燃速增加缓慢一些,三种粘合剂随压强提高其燃速增值为聚醚<HTPB<NEPE,即51%<61%<89%,显示出压强指数随之递增。虽然NEPE推进剂中的PEG仍为CH骨架,但被大量的硝酸酯“增塑”着,硝酸酯裂解产物基峰质量数44占峰面积72%,接近7倍于聚醚推进剂。其内在化学反应的差异造成了燃烧性能的不同,虽然RDX在配方中均占40%,裂解产物发生如此大的变化足以说明,NEPE少烟推进剂中 $-\text{O}-\text{NO}_2$ 、 $-\text{NO}_2$ 键断裂,主要是氮、氧元素之间的化学反应为主,进入气相反应区的分解产物主要是化学性质较稳定的 N_2O 和 CO_2 (与小部分粘合剂碎片反应结果)。因而在气相区反应弱,致使燃速低;当压强提高时,气相区离表面越近,单位体积内放热量增大,使更多的热反馈至燃面上,加快凝聚相热分解或燃烧速度,其活性分解产物 CH_2O , N_2O ,NO, ClO_3 , O_2 和C—H碎片间来不及进行氧化还原反应进入气相、使气相区的化学性能活泼的 NO_2 , ClO_3 等气体产物量猛增,在气相区快速燃烧,再反馈至燃面,加快凝聚相的热分解或燃烧,这样,低压下燃速低,随压强提高,燃速增加幅度大,导致燃速压强指数的提高。相反,聚醚推进剂上述现象弱,所以 n 值比NEPE推进剂低。

总之,以含能材料为基的NEPE少烟推进剂其凝聚相内的化学反应活性大,受压强的影响大,即压强升高时,其气相区的化学反应速度和凝聚相内的化学反应速度大大加快,其凝聚相相对推进剂燃速压强指数贡献大。因此,压强指数呈现出最高值。

参 考 文 献

- 1 徐浩星.不同粘合剂体系的RDX/AP推进剂燃速压强指数研究:[学位论文].襄樊:湖北红星化学研究所,1995
- 2 Liu huwei,etc. Investgation of thermal decomposition of HMX,RDX and NC by pyrolysis-gas chroratography. ICT,1988
- 3 Powlings,etc. The flame decomposition of some substituted etheyl nitrates. Combustion and Flame,1960,4