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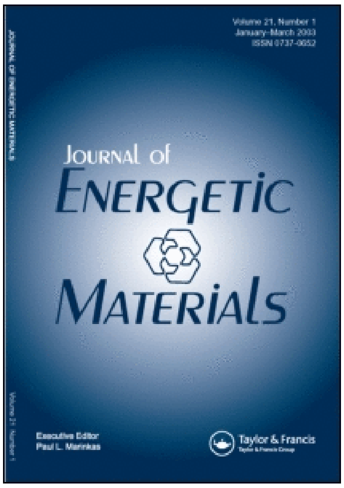

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Studies on Pre-Ignition Reactions of Hydrocarbon-Based Rocket Fuels Hypergolic with Red Fuming Nitric Acid as Oxidizer

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Studies on Pre-Ignition Reactions of Hydrocarbon-Based Rocket Fuels Hypergolic with Red Fuming Nitric Acid as Oxidizer

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Carene, norbornadiene, ethylidene norbornene, and furfuryl alcohol exhibit hypergolic ignition with red fuming nitric acid as oxidizer. Carene, when blended with norbornadiene, ethylidene norbornene, and furfuryl alcohol in appropriate proportions, exhibits synergistic hypergolic ignition with further decrease in ignition delay. In order to understand the probable mechanism of hypergolic ignition and synergy in ignition, various pre-ignition reactions have been studied by quenching the reactions and analyzing the intermediate products by Fourier transform infrared (FTIR) and gas chromatography–mass spectrometry (GC-MS) techniques. Based on the product analysis, the probable schemes of reactions have been proposed. Oxidation, nitration, and cationic polymerization appear to be the important pre-ignition reactions taking place simultaneously that are responsible for hypergolic ignition.

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Keywords: cationic polymerization, hypergolic ignition, ignition delay, pre-ignition reactions

Introduction

A number of fuel blends based on carene, cardanol, norbornadiene, ethylidenenorbornene (EN), furfuryl alcohol, and kerosene have been developed that exhibit synergistic hypergolic ignition with red fuming nitric acid (RFNA) as the oxidizer with ignition delays of less than 50 ms [1–6]. Various fuel blends were prepared by mixing two or more neat fuels in different weight proportions. The optimum compositions of blends were determined based on minimal ignition delay values measured at optimum oxidizer to fuel (O/F) weight ratios using Pino's ignition delay apparatus [5]. In order to understand the mechanism of hypergolic ignition and combustion of these fuel blends, various pre-ignition reactions have been quenched, products have been separated and characterized by different techniques, and possible pre-ignition schemes are proposed. A similar procedure was followed by various workers in the past to understand probable pre-ignition reactions for different solid and liquid hypergolic systems with RFNA as oxidizer [7–10].

Experimental

Materials

Carene was obtained from M/s Dujodwala Products Ltd., Mumbai, and used after distillation and appropriate stabilization. Ethylidene norbornene (Aldrich, Bangalore, India) was obtained and distilled before use. RFNA with HNO_3, 75%; N_2O_4, 22%; H_2O, 1.7%; H_3PO_4, 1%; and HF 0.3–0.5% and density of 1.56 g/cc was obtained from High Explosives Factory, Khadki, Pune.

Pre-Ignition Reaction Products of EN and Carene

In order to study the pre-ignition reactions, carene and EN were separately reacted with RFNA to get the reaction products for

Table 1

GCMS and IR data of various products separated from reaction mixture of EN and RFNA using hexane + 5% ethyl acetate as eluting solvent

Sr. no.	Retention time of various compounds with high concentration (min)	Molecular weights of major fragments in GC-MS chromatograms	Important IR peaks of the first fraction before GC-MS analysis
1	10.714	530, 282, 240, 254, 226, 268	1304–1260 cm^{-1}: ν C-O-NO_2 1376 cm^{-1}: ν C-NO_2 (Sy. Str.)
2	11.493	543, 268, 282, 254, 240, 226	1460 cm^{-1}: ν C=C (str) 1603.77 cm^{-1}: ν C-NO_2 (As. Str.)
3	12.169	708, 679, 281, 210, 679, 268, 252, 282	1719 cm^{-1}: ν C=O (str) $\left.\begin{matrix}2850\,\text{cm}^{-1}\\2954\,\text{cm}^{-1}\end{matrix}\right\}$: ν C-H (str) 2954 cm^{-1}

analysis. Carene/EN (~0.1 mol) was mixed with excess quantity of CCl_4 in a small beaker and slightly more than stoichiometric quantity of RFNA was added drop-wise to the reactant with constant stirring, thus dissipating heat. The stirring was continued for around 30 min after the addition. A semi-solid highly viscous brownish product was obtained in both cases. The reaction mixture was washed several times with CCl_4 to remove unreacted carene and EN and further with distilled water to remove the adhering acid. Further separation of the mixture of products in the case of EN was carried out by dissolving the reaction products in petroleum ether with a boiling point range of 60–80°C. The products were separated by column chromatography using column-grade silica gel as the stationary phase.

Table 2
GC-MS and IR data of various products separated from reaction mixture of EN and RFNA using hexane + 10% ethyl acetate as eluting solvent

Sr. no.	Retention time of various compounds with high concentration (min)	Molecular weights of major fragments in GC-MS chromatograms	Important IR peaks of the second fraction before GC-MS analysis
1	3.083	101	1047.98 cm^{-1}: ν O-C (str)
2	11.783	140, 224, 252, 238, 196	1242.71 cm^{-1}: ν C-O-C (str)
3	13.518	140, 154, 224, 252, 238	1374.23 cm^{-1}: ν C-H^{-} (bend)
4	15.868	281, 211, 197, 212	1743.29 cm^{-1}: ν RO-C=O (str) 2984.9 cm^{-1}: ν C-H (str)

Hexane was used as the eluting solvent. However, no product could be separated with pure hexane. The polarity of the eluting solvent was increased by adding ethyl acetate in 5, 10, and 15% weight proportion to hexane to collect first, second, and third fractions, respectively. Polarity was further increased to collect a few more fractions. Each fraction, being a mixture of different products, was analyzed by Fourier transform infrared (FTIR) and gas chromatography–mass spectrometry (GC-MS). However, in case of carene, such a procedure for separation of products by column chromatography was not found suitable and thus the reaction mixture was separated by adopting a selective solvent extraction scheme. The carene-based reaction mixture was extracted with benzene. The benzene-soluble and -insoluble fractions were separated. After evaporation of benzene, the products were collected and taken for analysis. The benzene-insoluble products were found to be completely soluble in acetone but insoluble in most of the common organic solvents like toluene, carbon tetrachloride (CCl_4), chloroform ($CHCl_3$), and dimethyl formamide (DMF). The benzene-insoluble products were taken separately for analysis.

Characterization of Pre-Ignition Reaction Products of EN and Careen

FTIR Spectral Analysis. FTIR spectra were recorded for various fractions of EN and carene using a Perkin Elmer spectrophotometer (model Spectrum One-3200; Bangalore, India). The spectra were recorded as smears prepared by using CCl_4. The IR spectral data for various fractions of reaction mixture of EN are included in Tables 1–3 along with GC-MS data. The IR spectral data along with pyrolysis-gas

Table 3

GC-MS and IR data of various products separated from reaction mixture of EN and RFNA using hexane + 15% ethyl acetate as eluting solvent

Sr. no.	Retention time of various compounds with high concentration (min)	Molecular weights of biggest fragments in GC-MS chromatograms	Important IR peaks of the third fraction before GC-MS analysis
1	11.375	252, 282, 281	1048 cm^{-1}: ν C-O (str)
2	11.633	207, 185, 200, 186	1247 cm^{-1}: ν C-O-C (str)
3	11.992	268, 281, 254, 282, 324	1374.24 cm^{-1}: ν C-H^- (bend) 1747 cm^{-1}: ν RO-C=O (str) 2940 cm^{-1}: ν C-H (str) 2984 cm^{-1}: ν C-H (str)

chromatography mass spectrometric (Py-GC-MS) data for benzene-soluble and -insoluble fractions from carene reaction mixture are included in Tables 4 and 5.

Gas Chromatography Coupled with Mass Spectrometry. Gas chromatograms were recorded for various fractions of EN using a Shimadzu gas chromatographic unit (model QP5050; Chennai, India). The column temperature was set to 200°C. The separated products from each fraction with different retention times were analyzed by mass spectrometry by electron impact technique using quadruple detectors. The GC-MS data for three fractions are given in Tables 1–3.

Table 4

Py-GC-MS data of various products separated from reaction mixture of carene and RFNA in benzene-soluble fraction

Sr. no.	Retention time of various compounds with high concentration (min)	Molecular weights of fragments in Py-GC-MS chromatogram	Important IR peaks of the benzene-soluble fraction before Py-GC-MS analysis
1	8.658	152, 154	958, 850, 752 cm^{-1}: ν C-O-C epoxy
2	9.150	122	1124 cm^{-1}: ν C-O-C
3	12.075	152	1373 cm^{-1}: ν C-NO_2 (Sy. Str.)
4	13.967	154	1557 cm^{-1}: ν C-NO_2 (As. Str.)
5	18.767	150	1640 cm^{-1}: ν C-O-NO_2 1712 cm^{-1}: ν C=O (str) 2974 cm^{-1}: ν C-H (str) 3036 cm^{-1}: ν C-H (epoxy) 3224 cm^{-1}: ν -OH

Table 5

Py-GC-MS data of various products separated from reaction mixture of carene and RFNA in benzene-insoluble fraction

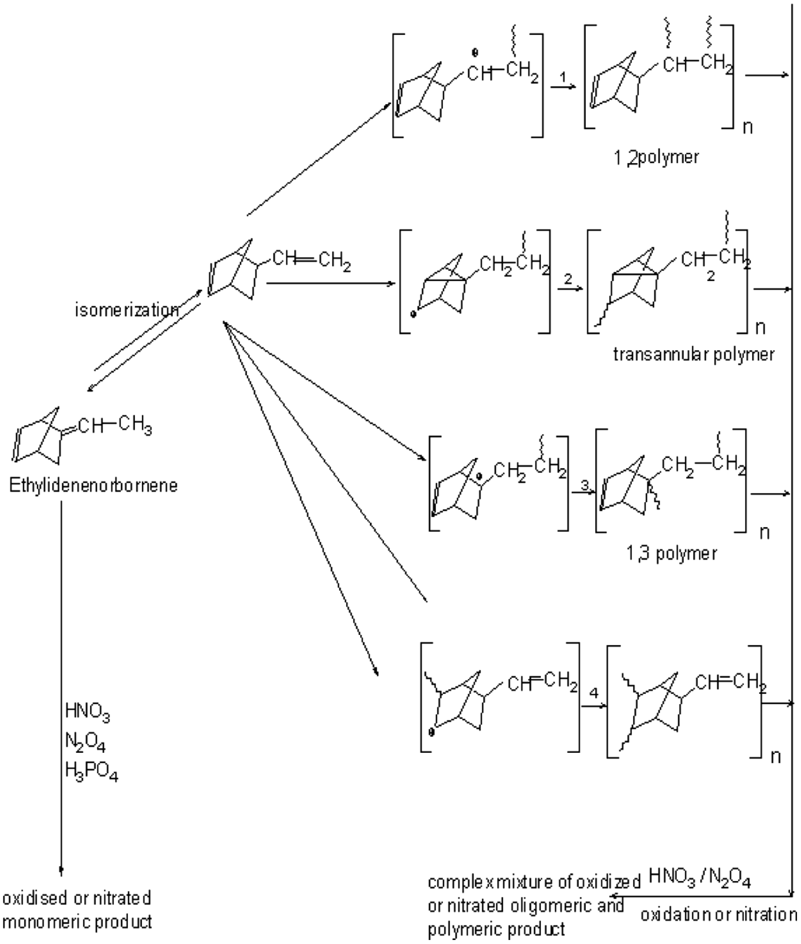
Sr. no.	Retention time of various compounds with high concentration (min)	Molecular weights of fragments in Py-GC-MS chromatogram	Important IR peaks of the benzene-insoluble fraction before Py-GC-MS analysis
1	1.908	150	850 cm^{-1}: ν C-O-C epoxy
2	5.15	61, 105	1230 cm^{-1}: ν C-O-C
3	8.717	134, 152	1372 cm^{-1}: ν C-NO_2 (Sy. Str.)
4	9.35	122	1557 cm^{-1}: ν C-NO_2 (As. Str.)
5	12.033	167	1640 cm^{-1}: ν C-O-NO_2
6	12.358	168	1703 cm^{-1}: ν C=O (str)
			2977 cm^{-1}: ν C-H (str)
			3428 cm^{-1}: ν -OH

Pyrolysis Coupled with Gas Chromatography Mass Spectrometry. In the case of the carene-based reaction mixture, separation of various products formed during the pre-ignition stage could not be done just by gas chromatography. The reaction products may be oligomerized, nitrated, and/or oxidized products having higher boiling and decomposition temperature. They could not be separated at the oven temperature, which was set at 200°C. It was then thought appropriate to pyrolyze them at a higher temperature of 250°C, and the pyrolyzed products with lower molecular weights, boiling points, and decomposition temperatures were separated by gas chromatography. Pyrolysis of benzene-soluble and -insoluble fractions was done using a Shimadzu pyrolyzer (model PYR 4 A) at 250°C. The products of pyrolysis of both fractions were fed to a Shimadzu gas chromatographic unit (model GC 17A) whose column temperature was programmed to 200°C. Helium was used as the carrier gas with a flow rate of 1.8 mL/min. The separated products from each fraction with different retention times were analyzed using a Shimadzu mass spectrometer (MSQP 5050A) by electron impact technique using quadruple detectors. The GC-MS data for two fractions are given in Tables 4 and 5.

Results and Discussion

Analysis of Pre-Ignition Reaction Products of EN and RFNA

The reaction products of ethylidene norbornene and red fuming nitric acid were separated as different fractions using the procedure discussed under experimental. The important IR spectral data are included in Tables 1–3 for first, second, and third fractions, respectively. Each fraction itself was a mixture of a few compounds containing similar functional groups. The IR data indicate that these fractions must contain different oxidized and nitrated products. However, assigning the precise chemical structure to any compound exclusively based on IR data is difficult. For further separation of the fractions, they were fed to a gas chromatograph. The molecular weights of the major fragments of the products separated with retention times of 10.71, 11.493, and 12.169 min with respect to fraction one are included in Table 1. Similar data for products separated from the second fraction (with retention times of 3.083, 11.783, 13.518, and 15.868 min) and from the third fraction (with retention times of 11.375, 11.633, and 11.992 min) are included in Tables 2 and 3, respectively. The general scheme of pre-ignition reactions for EN is represented in Scheme 1. It appears that EN first undergoes isomerization. A part of isomerized EN probably undergoes oxidation and/or nitration in the monomeric state, as indicated by the presence of m/z values of the separated products. However, it was also realized that some isomerized EN might have undergone highly exothermic oligomerization by cationic mechanism, in the presence of protonic acids like HF and H_3PO_4 present in RFNA. Ethylidene norbornene is known to undergo cationic oligomerization in the presence of mineral



Scheme 1. Pre-ignition reactions of isomerized EN with RFNA.

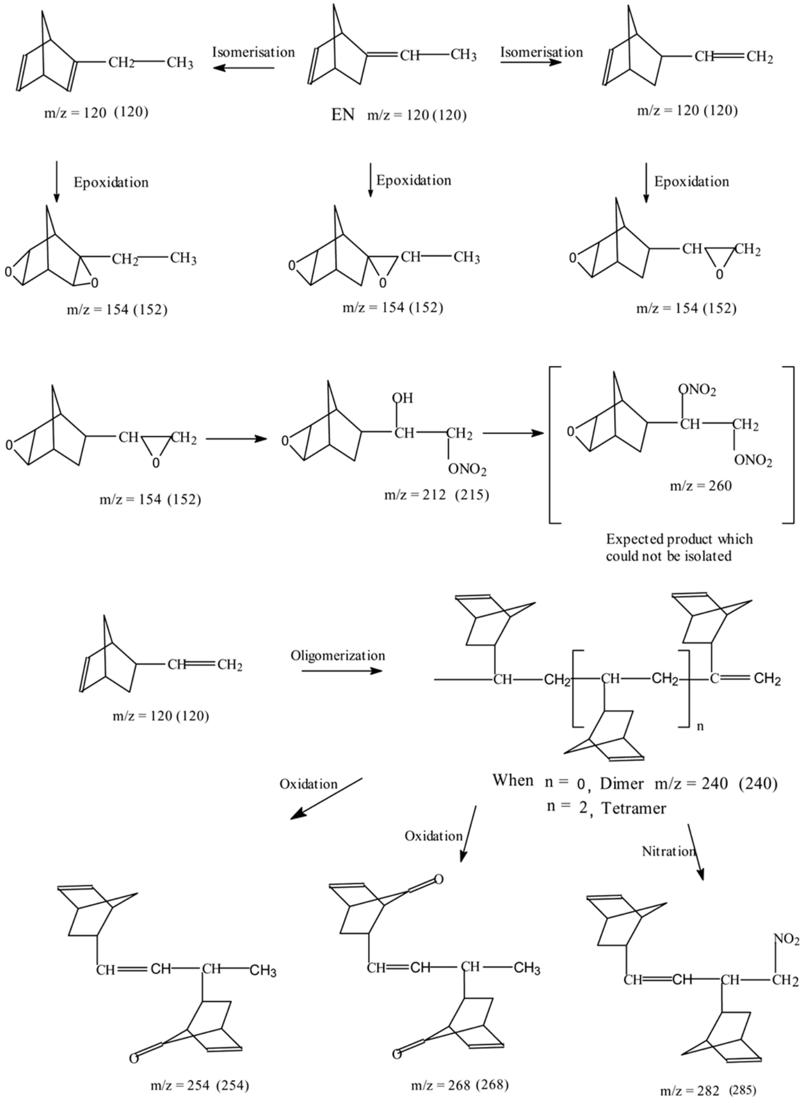
acids/Lewis acids [11]. Such oligomerized products are expected to undergo oxidation and/or nitration subsequently, forming a very complex mixture as supported by IR data. The total heat generated during oligomerization with subsequent oxidation and nitration may be responsible for hypergolic ignition. Interestingly, it was found that RFNA containing around 1% H_2SO_4 as catalyst decreases the ignition delay of carene and its blend with

EN. In a blend, these two fuels might be undergoing cationic oligomerization individually or cationic co-oligomerization, releasing more heat. These oligomerized products might undergo oxidation and nitration subsequently. Thus, the additional heat generated in cationic co-oligomerization may be responsible for synergy in ignition in the case of carene and EN blends [6,12]. Only a few products could be conclusively identified based on their m/z data, which are shown in Scheme 2 with their most probable structures.

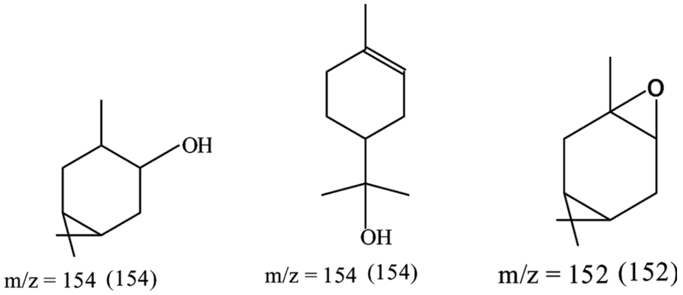
Analysis of Pre-Ignition Reaction Products of Carene and RFNA

The pre-ignition reaction products in the case of carene were separated using benzene as the extracting solvent as mentioned in the Experimental section. The benzene-soluble and -insoluble fractions were the complex mixtures of monomeric and oligomerized oxidized and/or nitrated products. They were subjected to pyrolysis. The pyrolyzed products were separated by gas chromatography and then analyzed by mass spectrometry. Table 4 includes pyrolyzed GC-MS and IR data for fraction 1. The IR data indicate that the mixture may contain oxidized, nitro, and nitrated products. Table 4 also includes the retention times of various pyrolyzed products separated from fraction 1 by gas chromatography, along with their m/z values. Table 5 contains similar data for the benzene-insoluble fraction.

The various fragments of pyrolyzed products were separated by gas chromatography and analysed by their m/z values. The probable structures that could be assigned to them are shown in Schemes 3 and 4 for benzene-soluble and -insoluble fractions, respectively. The reaction products shown in Schemes 3 and 4 indicate that carene must have undergone isomerization by opening of a cyclopropane ring in the presence of protonic acids like HF and H_3PO_4 through a cationic mechanism. Sulphuric acid also exhibits similar results as reported by us earlier and also by other workers [13–15]. It can be highlighted at this stage that carene exhibits hypergolic ignition with shorter ignition delay times when RFNA is mixed with 1% H_2SO_4. The decrease

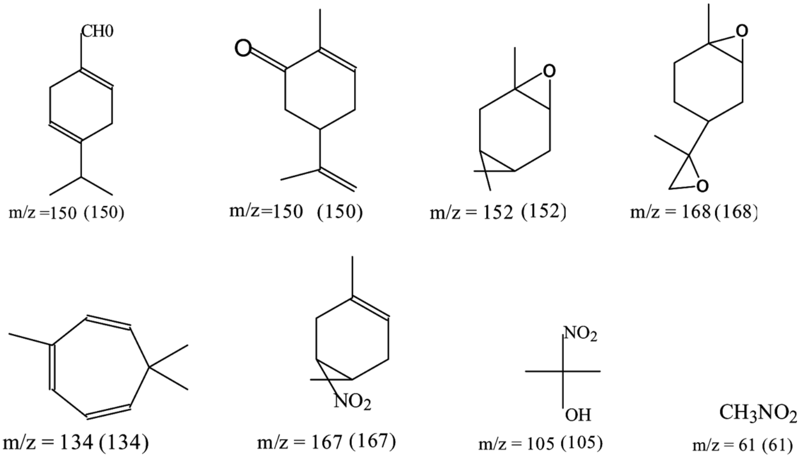


Scheme 2. Probable structures of the products identified based on mass spectral data.



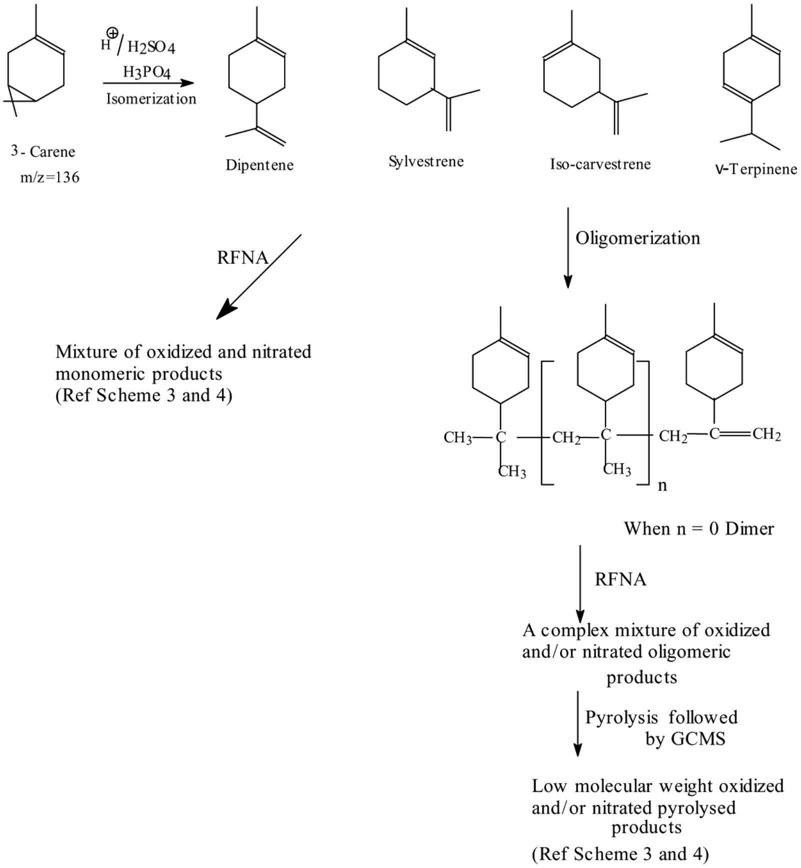
Scheme 3. Pre-ignition products identified from benzene-soluble fraction.

in ignition delay may be due to fast cationic polymerization in the presence of H_2SO_4. Some isomerized carene molecules might have undergone oxidation and/or nitration in monomeric state and some might have undergone oligomerization. These oligomerized products may in turn react with nitric acid, thus forming a complex mixture of oxidized and or nitrated products. However, such nitrated and oxidized oligomerized products could not be identified by GC-MS alone. These products were



Scheme 4. Pre-ignition products identified from benzene-insoluble fraction.

subjected to pyrolysis and the pyrolyzed species were fed to the mass spectrometer. The fragments formed were analyzed by their m/z values. Because the reaction products are very complex mixtures containing a large number of species, it is difficult to specify the exact sequence of reactions and the actual products formed. However, a general scheme of reactions is represented in Scheme 5. The structures of the probable products are confirmed by their m/z values.



Scheme 5. General scheme of pre-ignition reactions of carene with RFNA.

Conclusion

A number of fuel blends based on carene, norbornadiene, ethylidene norbornene, furfuryl alcohol, and kerosene have been developed that hypergolically ignite with red fuming nitric acid as oxidizer. The fuel blends based on carene and ethylidene norbornene in 10:90 and 25:75 weight proportion were found to be more promising based on their ignition delay and theoretical performance data. For experimental validation of performance parameters, these fuel blends were statically test fired at 75 kgf thrust level. They exhibited density impulse values higher than the majority of the fuel blends presently being used for missile and launch vehicle application. The fuel blends are environment friendly and cost effective as well.

Oxidation, nitration, and cationic polymerization occurring simultaneously were proposed and proved to be important pre-ignition reactions responsible for hypergolic ignition. For better understanding of pre-ignition reactions, neat fuels like carene and ethylidene norbornene were reacted with red fuming nitric acid in CCl_4 medium with constant stirring and dissipating heat generated to obtain a complex mixture of reaction products. Various products formed were separated either by a column chromatographic or by a selective solvent extraction technique. The separated products were mixtures of structurally similar compounds having identical functional groups. Further separation was carried out either by a gas chromatographic or a pyrolysis gas chromatographic technique. The products of ethylidene norbornene were identified based on FTIR and GC-MS data. In the case of carene, however, FTIR and Py-GC-MS data were used for the identification of products. The general schemes of pre-ignition reactions for ethylidene norbornene and carene were presented based on their product analysis. It is thus concluded that ethylidene norbornene and carene first undergo exothermic isomerization in the presence of red fuming nitric acid. The isomerized products subsequently undergo oligomerization followed by oxidation and or nitration, thus forming a highly complex mixture of oxidized and or nitrated products. Alternatively, the isomerized products in a monomeric state may undergo oxidation and/or nitration and subsequently undergo partial or complete oligomerization again, forming the complex mixture. A number of oxidized and nitrated monomeric and oligomeric products have been identified by their m/z values and probable structures have been assigned to them.

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