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Aluminum Alkyl Derivatives—Ignition and Combustion Enhancers for Supersonic Combustors

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The work in this article was based on adapting an apparatus and procedure developed for rating the ignition quality of fuels for diesel engines. Aluminum alkyls and various Lewis-base adducts of these materials, both neat and mixed 50/50 with pure JP-10 hydrocarbon, were injected into the combustion bomb using a high-pressure injection system. The bomb was precharged with air that was set at various initial temperatures and pressures for constant oxygen density. The ignition delay times were determined for the test materials at these different initial conditions. The data are presented in absolute terms as well as comparisons with the parent alkyls. The relative heats of reaction of the various test materials were estimated based on a computation of the heat release, using the pressure data recorded during combustion in the bomb. In addition, the global reaction rates for each material were compared at a selected temperature and pressure.

Introduction

THE current trend in aircraft design appears to be the extension of the operating envelope of the next generation of high-performance aircraft gas turbine engines into the $M = 4$–7 range. Flight at these high velocities in the atmosphere creates several problems that have, until very recently, been considered to be insurmountable in practical systems. The first problem involves the high stagnation temperatures that are encountered at the high velocities being considered. Either active airframe cooling and/or exotic materials are required to overcome the high surface temperatures. Several different approaches to the heating problem are being examined in detail in other studies. The subject of this article is the second problem, that supersonic combustor designs will probably be required in order to achieve the needed reaction rates in a reasonably sized combustor.

Development of hypervelocity, air-breathing vehicles depends on the ability to design combustion systems that permit complete combustion in the supersonic flow of the combustor. That is, supersonic combustion requires short ignition delay times and fast reaction rates; the types of fuel that meet these stringent requirements of supersonic combustion are quite limited. Up to this point, hydrogen is the only fuel that provides the short ignition delay time and fast reaction rates required of supersonic combustion. However, the hazards associated with using hydrogen as a fuel are substantial, and hydrogen may not be suitable for use in aircraft due to its low energy density. Recent suggestions for supersonic combustion systems include the onboard production of hydrogen from hydrocarbons or fuel additives that can enhance the ignition and combustion of some hydrocarbon fuels.

Another fuel-additive approach, which is the focus of this research, is the use of pyrophorics to shorten the ignition delay time and to increase the energy density of the fuel. Pyrophoric organometallic compounds may also provide an ignition source and flame stabilizing mechanism within the combustor, thus permitting the use of hydrocarbon fuels in supersonic combustion systems. Triethylaluminum (TEA) and trimethylaluminum (TMA), which are very aggressive pyrophoric compounds, have been suggested for this application due to their high energy density and reactivity.

Development of such a supersonic combustor requires the development of a method to safely store and handle large quantities of the aluminum alkyls. Microencapsulation of triethylaluminum was examined[1,2] as a promising candidate for the safe storage and handling of large quantities of TEA. Triethylaluminum was selected by NASA as the demonstration fuel for microencapsulation because it ranks high in reactivity and energy density and is readily available. Also, the vapor pressure of TEA is low enough (0.025 mmHg at 25°C) such that it can be handled at normal ambient storage temperature and, more importantly, is low enough for assured containment at the allowed peak ambient temperature (1.5 mmHg at 70°C). Also, TEA is slightly less toxic than boron- or halogen-containing compounds. Alcoholysis of TEA was investigated[1] as a means of preheating TEA with hydrocarbon fuel carrier (and melting of crushed capsules) to enhance injection with vaporization.

Background

Several different traditional and exotic encapsulating materials were examined[2] in an effort to develop a procedure for encapsulating the TEA that would meet all the handling and safety requirements for such a fuel additive. As the encapsulation effort proceeded, it became increasingly obvious that successful microencapsulation of TEA is limited by the availability of an appropriate material. It was felt that an extensive polymer synthesis development effort would be required to produce a material that would contain the TEA within the specified parameters, which included the capsule size, the mass ratio of encapsulating material to TEA, capsule strength, and capsule storage life.

To mitigate the hazards associated with handling these alkyls, complexes of TMA and TEA with Lewis bases were synthesized. The chemical reactivity of aluminum alkyls is dominated by coordinative unsaturation and electron deficiency, while their solubility properties are dominated by the pendent alkyl groups,[3] and so complexes of aluminum alkyls with Lewis bases should be significantly less reactive, easier to handle, and more amenable to encapsulation. Many of these Lewis base adducts are thermally liable, and so will dissociate to liberate the aluminum alkyl at elevated temper-

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ature. It was felt that the use of such complexes would significantly broaden the range of candidate encapsulation materials, or even make encapsulation unnecessary, if the adducts were found to be nonpyrophoric under ambient conditions.

Several different adducts were formed with both TEA and TMA. Each of these materials was evaluated in both drop experiments and continuous flow reactor experiments. These experiments were designed to provide a quick screening of the pyrophoric nature and the combustion characteristics of each material. The results of these tests did indicate that some of the materials were indeed safer to handle and did appear to have acceptable ignition and combustion characteristics. These initial experiments did not, however, quantitatively address the effects of the synthesis on the ignition quality, the energy density, and the reactivity of the adducts in an environment at elevated temperature and pressure.

Objectives

The objective of the work reported in this article was to provide at least comparative data for the ignition quality, the energy content, and the reaction rates of several different adducts of both TEA and TMA, as compared to the corresponding properties for the pure parent compounds.

Experimental Apparatus and Procedures

Apparatus

The experimental apparatus was developed to study the ignition characteristics of hydrocarbon fuels. The design of the facility and its application to hydrocarbon fuels has been presented by Ryan and Stapper[4] and Ryan.[5] The facility consists of a constant-volume combustion apparatus (CVCA), a single-shot fuel injection system, and a data acquisition and reduction system. The CVCA consists of a stainless steel cylinder machined to accept a water-cooled piezoelectric pressure transducer at one end and a fuel injection nozzle at the other end. The internal geometry of the CVCA is cylindrical, with a diameter of 5 cm and an approximate length of 10 cm. The actual volume of the combustion chamber is 192 cm^3. The CVCA is equipped with electrical resistance heaters to heat the vessel walls as well as the contents of the combustion chamber. The internal temperature is monitored with an unshielded thermocouple probe, and an automatic controller controls the temperature of the apparatus.

The fuel injection system consists of an inward opening pintle nozzle coupled through a short length of high-pressure injection tubing to a 9.0-mm barrel and plunger assembly. The pumping element is activated pneumatically for a single-shot injection. The performance of the injection system, in terms of drop-size distribution and spray geometry, have been well documented.[4,6,7] The combustion chamber geometry and dimensions and the injection system design were matched to prevent fuel impingement and to ensure that appropriate air/fuel ratios are maintained. The repeatability of the injection system performance is monitored through continual observation of the injection line pressure and the nozzle needle lift characteristics as recorded using the appropriate transducers mounted in the injection system.

The fuel supply reservoir for the injection system consists of a 200-ml, vertical cylindrically shaped stainless pressure vessel. In the case of hydrocarbon fuels, the fuel is simply poured into the vessel, a free piston is installed above the fluid, and nitrogen is used to force the fuel into the injection pump assembly. The test materials in these experiments, because of their potential pyrophoric nature, were always stored in nitrogen-sealed vessels. The materials were introduced into the fuel reservoir through a fitting at the bottom of the vessel using nitrogen pressure to force the material into the reservoir. The test materials were, therefore, always sealed in pressurized nitrogen environments.

Data Acquisition and Reduction

The data acquisition and reduction system consists of a digital oscilloscope and PC-based data reduction software. Three channels of data were recorded during each experiment. One channel consisted of the output from a proximeter sensor used to detect the motion of the needle valve in the fuel injection nozzle, this output was used to mark the start of injection. The second data channel consisted of the output from a pressure transducer installed in the high-pressure tubing between the injection pump and the nozzle, this output was used to monitor the injection pressure as a diagnostic of the injection process. The third channel consisted of the output from the pressure transducer installed in the CVCA combustion chamber, this output provided the combustion pressure data that was used to compute the ignition delay times, the cumulative heat release, and peak heat release rate.

The technique for measuring the ignition delay used in the experiments consists basically of the development and application of a technique suggested by Hurn et al.[8] and Yu et al.[9] As adapted and applied to the combustion apparatus, the technique consists of measuring the pressure change that occurs in the CVCA during the injection, ignition, and combustion events. The pressure in the combustion chamber drops immediately upon injection, due to the cooling effect of the evaporating fuel. The time from the start of injection to the point where the pressure reaches the minimum has been defined as the physical delay time.[5] The total ignition delay time is generally defined in terms of the time at which the pressure recovers to the baseline value.

The heat release rates were computed from the CVCA combustion chamber pressure using a first law analysis and assuming ideal gas and no heat transfer during combustion. The heat release rate curves were integrated over the duration of combustion to arrive at the cumulative heat release.

Test Materials

The test materials included TEA, TMA, JP-10 (cyclopentadiene), two adducts of TMA, four adducts of TEA, and 50/50 mass blends of each in JP-10. JP-10 was selected as the base hydrocarbon fuel. Other hydrocarbons could be used, and in fact, optimized for ignition quality. The ignition delay characteristics of JP-10 are much worse (longer delay times) than those of JP-4. The adducts were synthesized through the addition of a Lewis base (electron donor) to the appropriate alkyl triethylaluminum (TEA) or trimethylaluminum (TMA) in an inert solvent (e.g., hexane) under anhydrous and anaerobic conditions.[10,11] The compounds are isolated by fractional distillation under reduced pressure. Both the starting alkyls exhibit predominantly dimeric structures in solution at room temperature.[3,12] Addition of the Lewis base breaks up the dimer to form a coordinatively and electronically saturated tetrahedral, four-coordinate species

$$\mathrm{Al_2R6} + 2\mathrm{ER}'_x \rightarrow 2\mathrm{R_3Al}\cdot\mathrm{ER}'_x \qquad (1)$$

where E = O, N; R, R′ = alkyl, aryl, $x = 2$ when E = O and $x = 3$ when E = N.

The TMA and TEA are pyrophoric (burst into flame on exposure to ambient air), and their Lewis base adducts are substantially less reactive at room temperature. Although some do smoke on exposure to air and others burst into flame if poured into bulk water, they are, as a class of material, considerably easier to handle than unmodified TMA or TEA. While they do not exhibit pyrophoric behavior at room temperature, the adducts dissociate at elevated temperature (roughly 100°C) to liberate the alkyl and restore pyrophoricity. The TMA adducts are listed in Table 1, and the TEA adducts are listed in Table 2.

Test Procedures

Transfer of the test material into the fuel reservoir was the most difficult aspect of the preparations for the experiments.

Table 1 Lewis base adducts of trimethylaluminum (TMA-37.4% Al)

Lewis base	Symbol	% Al	Comments
Diethylether	(TMA.OET$_2$)	18.5	Clear liquid, smokes on contact with air, not pyrophoric
Tetrahydrofuran	(TMA.THF)	18.7	Clear liquid

Table 2 Lewis base adducts of trimethylaluminum (TMA-23.6% Al)

Lewis base	Symbol	% Al	Comments
Trimethylamine	(TEA.NME 3)	15.6	Clear liquid smokes in air
Diethylether	(TEA.OET$_2$)	14.3	Clear liquid
Diisopropyl	(TEA.PRI$_2$)	12.2	Clear liquid
Di-n-butyl ether	(TEA.OBU$_2$)	11.0	Clear liquid

In addition, approximately 25–50 ml of material was lost during each fuel change to flush the system. It was therefore decided to load each material only one time and change the test conditions and complete the test for each material separately.

The test variables, in addition to the test material, were the initial air pressure and temperature in the CVCA combustion chamber. Initially, the experiments were performed at 700, 755, and 855 K. It was found, however, that the ignition delay times for most of the test materials were very short at these test conditions. The test matrix was therefore expanded to include tests for several materials at temperatures of 645, 590, 535, 480, 425, 370, and 315 K, in order to provide sufficient variation in the delay time to demonstrate any temperature effects. The air pressure in the combustion chamber was changed at each test condition so that all tests were performed at the same air density of 0.015 kg/l.

A significant data base of ignition delay times of several hydrocarbons has been developed in previous projects. The experience of these several thousand experiments dictates that a baseline run be performed each day to verify the repeatability (±0.05 ms at 855 K) of the experimental apparatus and procedures. Therefore, a calibration run was performed using hexadecene at an initial condition of 855 K. The calibration run was then compared to the baseline, and if there were no significant differences, the fuel system was then purged and charged with the test material. The first experiment was then performed by injecting the test material into the 855 K air. The experiments were repeated three times at each test temperature, and data for all runs stored on discs for retrieval and reduction at a later time. All experiments were performed by injecting the same volume, 0.08 ml, of test material.

Results and Discussions

General Observations from the Pressure-Time Histories

The primary objective of this work was to determine if there are penalties involved in transforming the pyrophoric aluminum alkyls into more stable adducts. The results of drop and flow reactor tests indicated that while neat TEA and TMA are pyrophoric, only the TMA is pyrophoric when blended 50/50 v/v in JP-10. Storage stability is acceptable if the blends are not contaminated with oxygen or water and the temperature is maintained at a reasonable level. The adducts of both TEA and TMA are less reactive than the parent materials, and they were not pyrophoric when blended with JP-10. The possible penalties in using the adducts could include an increase in the ignition delay times, a decrease in the energy contents, and a decrease in the reaction rates relative to the parent materials. It was felt, however, that the adducts would dissociate in a slightly endothermic process to the base alkyl quickly in the combustor environment, and the ignition delay penalty would be small. As will be shown, the results of these experiments did demonstrate that the penalties were negligible. In fact, it appears that concentrations lower than 50% may be as effective as the higher concentrations.

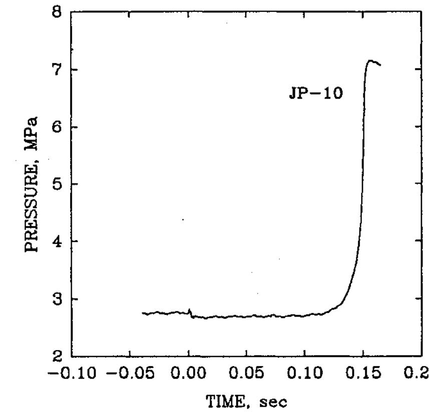

Fig. 1 Pressure-time history for JP-10. Initial temperature of 645 K.

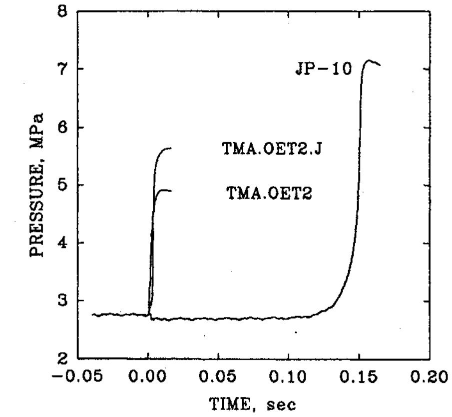

Fig. 2 Pressure-time histories for the diethylether adduct of TMA, its 50/50 blend in JP-10, and neat JP-10. Initial temperature of 645 K.

The primary data obtained during the CVCA experiments were the pressure-time histories measured as the various materials were injected into controlled pressure and temperature air. As a reminder, the material and the initial temperature were the primary independent variables in the experiment. The pressure was set at each initial temperature so that all experiments were performed at constant air density.

The initial experiments were performed at 645, 700, 755, and 855 K using JP-10. The pressure-time histories for the JP-10 at 645 K are presented in Fig. 1. As with other hydrocarbons tested in this apparatus,[4] the pressure initially drops, due to the cooling effect of the fuel vaporization process; this is clearly shown at the 645 K test condition. The physical delay time (fuel injection and evaporation time) can be defined in terms of the elapsed time from the start of injection to the minimum of the pressure-time history. The start of

Table 3 Averages vs function of temperature

Fuel (sample), K	Ignition delay time, ms									
	315	370	425	480	535	590	645	700	755	855
TMA	0.64	0.62	0.62	0.57	0.57	—	0.55	—	—	—
TMA.JP10	—	—	0.63	0.60	0.49	0.57	0.57	0.57	0.53	—
TMA.THF.N	—	—	1.49	—	—	0.59	0.55	0.50	—	0.483
TMA.THF.J[a]	—	—	—	—	—	0.67	0.63	0.54	0.56	0.533
TMA.OET2.N	—	—	—	—	—	0.57	0.52	0.54	0.52	0.51
TMA.OET2.J	—	—	—	—	—	0.42	0.61	0.61	0.56	0.57
TEA	—	0.63	0.59	0.58	0.56	—	0.51	—	—	—
TEA.JP10	—	—	—	—	—	0.58	0.56	0.55	0.52	—
TEA.PRI20.N	—	—	—	—	—	0.52	0.48	0.48	0.46	0.47
TEA.OBU2.N	—	—	—	—	—	0.54	0.50	0.51	0.48	0.50
TEA.OBU2.J	—	—	—	—	—	0.62	0.56	0.51	0.51	0.53
TEA.NME3.N	—	—	—	—	—	0.58	0.55	0.56	0.52	0.50
TEA.NME3.J	—	—	—	—	—	0.68	0.61	0.56	0.60	0.61
TEA.OET2.N	—	—	—	—	—	0.60	0.58	0.58	0.56	0.63
TEA.OET2.J	—	—	—	—	—	0.62	0.61	—	0.65	0.59
JP-10.N	—	—	—	—	—	505	105	23.0	5.68	5.16

[a] .J designates neat material.

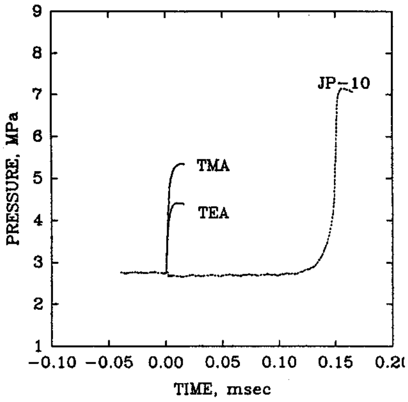

Fig. 3 Pressure-time histories for neat TEA, TMA, and JP-10. Initial temperature of 645 K.

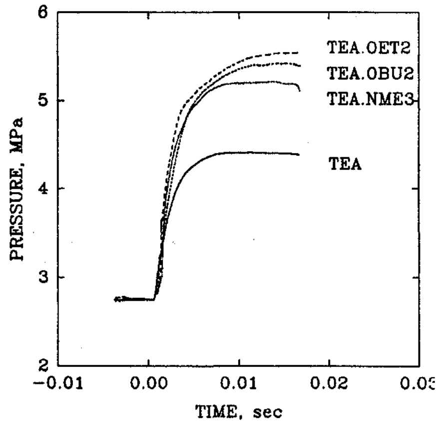

Fig. 4 Pressure-time histories for the TEA-based test materials. Initial temperatures of 645 K. (See discussion regarding TEA results.)

Table 4 Arrhenius expressions for the ignition delay times

Material	Delay time = $A \exp(B/T)$ A	Delay time = $A \exp(B/T)$ B	Apparent activation energy, kcal/mole
TMA	0.457	117	0.23
TMA.JP-10	0.458	133	0.26
TMA.THF	0.291	409	0.81
TMA.THF.J[a]	0.294	477	0.95
TMA.OET2	0.411	180	0.36
TMA.OET2.J	0.443	221	0.44
TEA	0.395	159	0.32
TEA.JP-10	0.368	270	0.53
TEA.OBU2	0.406	154	0.31
TEA.OBU2.J	0.334	340	0.67
TEA.NME3	0.356	280	0.56
TEA.NME3.J	0.456	205	0.41
TEA.OET2	0.453	165	0.33
TEA.OET2.J	0.526	92.6	0.18
JP-10	4.15×10^{-6}	10,970	21.8

[a] .J = 50/50 mass blend in JP-10.

injection is determined using a sensor that detects the motion of the valve in the injection nozzle.

A small positive spike at the start of the evaporation pressure drop on the pressure-time trace provides a mark of the start of injection. In the case of JP-10, the physical delay time is on the order of 1 ms at the 645 K test condition. The neat metal alkyls and the adducts did not display this pressure drop, even at initial temperatures as low as 315 K. This is shown in Fig. 2 at an initial temperature of 645 K where the pressure-time histories for the diethylether adduct of TMA, the 50/50 blend of the diethylether adduct of TMA in JP-10, and neat JP-10 are presented. Please note that the "J" suffix designates the 50/50 blends and the "N" suffix designates neat material. In addition, the results in Fig. 2 clearly demonstrate that the ignition delay time of the adducts and the blends are significantly shorter than the neat JP-10. The overall combustion times are also generally an order of magnitude shorter than those of the neat JP-10, even at the higher initial temperatures.

The pressure-time histories for the neat materials (TEA, TMA, and JP-10) are shown in Fig. 3 at an initial temperature of 645 K. The ignition delay time for the alkyls are almost identical and are an order of magnitude shorter than the corresponding delay for the JP-10. The peak reaction rates, as indicated by the peak slopes of the pressure traces are also very similar for the alkyls, but were generally found to be somewhat lower than that of the JP-10.

The peak pressure also provides a measure of the total energy released during the reaction. Based simply on the peak pressure in the CVCA, it was generally observed that the heats of reaction of the neat alkyls are approximately 20–30% lower than that of JP-10, and the adducts are from 40–60% lower. These results for the alkyls are somewhat lower than expected, based on the constant pressure heats of combustion reported in the literature. It should be remembered, however, that these experiments were performed at constant volume, and at initial pressures ranging from 1.44 to 3.65 MPa.

The impact of forming the various adducts of TEA is demonstrated in Fig. 4, where the pressure histories for these materials and the neat TEA are presented. The ignition delay

Table 5 Properties and relative total heat release and peak heat release rates for the test materials

Material	Specific gravity	Relative[a] total heat release	Relative[a] peak heat release	Total reaction time, ms
TMA	0.752	1.00	1.0	14.8
TMA.JP-10	0.835	0.89	——	16.7
TMA.THF	1.10	0.54	0.59	16.7
TMA.THF.J[b]	1.01	0.80	——	10.0
TMA.OET2	1.03	0.61	0.89	11.4
TMA.OET2.J	0.98	0.87	——	16.7
TEA	0.837	1.00	1.00	10.6
TEA.JP-10	0.89	0.99	——	13.6
TEA.PRI2	——	——	——	——
TEA.OBU2	1.09	0.63	0.39	13.7
TEA.OBU2.J	1.01	0.79	——	14.6
TEA.NME3	1.05	0.54	0.68	14.9
TEA.NME3.J	0.99	0.87	——	13.9
TEA.OET2	1.03	0.78	0.49	15.4
TEA.OET2.J	0.98	——	——	——
JP-10	0.94	1.00	1.00	156

[a] Relative to the corresponding data for the parent materials.
[b] .J = 50/50 mass blend in JP-10.

times are very similar for all the materials. In addition, the peak pressures, and therefore, the heats of reaction of all the material were very similar. The exception was the TEA, which had a much lower peak pressure. It is believed that the injection system was set incorrectly for TEA at this test condition because, at the other test conditions, the peak pressures for the TEA were in-line with the data for the other materials.

Ignition Delay Data

The ignition delay times and the peak pressure for all the material are summarized in Table 3 for all the test conditions. The results represent the averages of the three experiments that were performed at each test condition for each material. Two readily apparent and important observations can be made regarding the data. First, the ignition delay times for the aluminum alkyls and the adducts are all significantly lower than the corresponding results for JP-10. Second, the ignition delay times for the alkyls and the adducts are not as temperature-dependent as that of JP-10, which is similar to those of other hydrocarbon materials as measured in the same apparatus.[13]

The ignition delay data for all the materials were plotted as Arrhenius functions of temperature. The difference in temperature dependence is demonstrated by the two-order of magnitude difference in the apparent activation energies. The Arrhenius coefficients and the apparent activation energies for ignition of the test materials are summarized in Table 4. The ignition activation energy for JP-10 is approximately 50% of that reported by Spadaccini and Tevelde[14] for a variety of hydrocarbon fuels. It is in good agreement, however, with the results presented by both Ryan and Callahan[13] and Siebers and Dyer.[15] It is felt that the absolute numbers are not as important as the fact that the activation energies of ignition are consistently two-orders of magnitude lower for the alkyl and adduct containing materials than that of JP-10.

Thermochemical Properties

It is possible to determine the heat of combustion and the global reaction rate as a function of temperature and pressure-based first law analysis performed in conjunction with the pressure-time histories obtained in the CVCA. The accuracy of the heat of combustion calculation depends on the precision of the fuel system in injecting the desired, or at least a known, mass of fuel. It is based on an assumption of no heat transfer during combustion. It is also dependent on the quality of the available property data for the test material, in particular the specific heats, the heats of vaporization and fusion, and the densities. This type of property data was not available for the adducts of the aluminum alkyls. It was therefore decided to present the available data on a relative basis, allowing at least some measure of comparison of the various materials.

The results of the first law analysis are presented in Table 5 as the relative total heat release, based on the peak pressures recorded for each material at the 645 K test condition. This test condition was selected for the comparison because it was the only condition at which all the materials were tested (see Table 2). The results are presented relative to the corresponding parent material. Based on this analysis, the adducts liberated from 54 to 78% of the energy liberated by the corresponding parent aluminum alkyl. The 50/50 blends apparently liberated from 79 to 89% of the energy released by the individual constituents. The percentages for the blends should be 100 if the heat transfer assumptions and the injected masses are consistent. This inconsistence in the data is not understood, but it is possible that the alkyl and adduct containing materials have higher heat transfer rates than the JP-10 due to radiation heat transfer from the solid products of combustion. Using this possibility to grossly adjust the results for the adducts, it appears that the heats of combustion of the adducts are in the range of 61–85% of those of the corresponding alkyl.

Also presented in Table 5 are the relative peak heat release rates, based again on a first law analysis of the pressure data. In this case the peak rate is based on the peak slope of the pressure-time histories. It appears from these calculations that the peak reaction rates of the adducts are in the range of 39–89% of the parent alkyl. In addition, the peak rates for both the adducts and the neat alkyls were found to be lower than those for JP-10, but the blends generally had higher peak rates than the neat alkyl.

The last column of data presented in Table 5 is probably the most important in terms of defining the effects of the various additives on the overall reaction rate. The total reaction time is defined as the time from the start of fuel injection to the point of peak pressure. The results show that the addition of the additive reduces the overall reaction time by one order of magnitude. This result was consistent at all test conditions, as reflected in the Arrhenius rate equations presented in Table 4.

Summary

The results of the experiments described in this article indicate the aluminum alkyls, and more stable derivatives of these alkyls all significantly reduce the ignition delay time and the total reaction time of JP-10. The temperature dependence of ignition delay time and the total reaction times of the blends of the adducts in JP-10 are significantly lower (two- and one-order of magnitude, respectively) than the neat JP-10.

Drop and flow reactor studies have shown that the adducts are much easier to handle than the neat alkyls. The adducts also appear to have excellent storage stability as long as contamination and overheating are prevented. The ignition delay measurements and the total reaction time measurements indicate that adducts function very similar to the neat alkyls in the combustion process to reduce the overall reaction times. The only apparent drawback to the use of the alkyls is a possible penalty in the heats of combustion. It should be noted that interpretation of the reported data for the reaction rates and the heats of reaction are gross and meant only to show trends. Future work will include experiments at lower concentrations of the adducts and measurements of the actual heats of combustion, and much more precise measurements of the reaction rates of selected adducts.

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