United States Patent Office 3,405,130 Patented Oct. 8, 1968

3,405,130

ADDUCTS OF ALUMINUM, BERYLLIUM AND ZIRCONIUM BOROHYDRIDES WITH NITROGEN AND/OR OXYGEN-CONTAINING LIGANDS

John N. Hogsett, Charleston, Albert Khuri, South Charleston, and Helmut W. Schulz, Charleston, W. Va., assignors to Union Carbide Corporation, a corporation of New York

No Drawing. Filed Oct. 25, 1961, Ser. No. 147,438
17 Claims. (Cl. 260—242)

This invention relates to the preparation of adducts of metal borohydride with a ligand composed solely of carbon, hydrogen, etheric oxygen, and amino nitrogen atoms. In various aspects, the invention relates to liquid propellant and solid propellant systems which utilize said novel adducts as a fuel component therein.

In recent years, industry has been actively engaged in the search for fuels which are suitable for propellant systems. While various fuel compositions have been suggested and tried for such purposes, limited success has been achieved in view of the exacting requirements of the art. Among the more important characteristics of, for example, a liquid fuel can be listed (1) high specific impulse, (2) relatively high density, (3) liquid state over a wide temperature range, (4) low freezing point, (5) hypergolicity with common oxidizers, and (6) ease of handling without undue hazard. Since the above enumerated characteristics are not all consistent with one another, a balance or compromise must be made.

Metal borohydrides, such as aluminum borohydride, beryllium borohydride, and zirconium borohydride, because of their potentially high heat release, have aroused some interest in the past as a fuel in rocket systems. However, the violent chemical reactivity and thermal instability of, for example, aluminum borohydride and beryllium borohydride, have created handling and storage problems which have precluded their serious consideration as storable rocket fuels. For instance, aluminum borohydride and beryllium borohydride inflame violently in air and react vigorously with water. Moreover, beryllium borohydride suffers from the disadvantage of being extremely toxic. Then density of aluminum borohydride being 0.55 gram/milliliter, at 25° C., further detracts from its desirability as a rocket fuel since large tankage would be required to sustain long range rocket flights. The disadvantages which result from increased missile weight due to large fuel storage tanks are obvious. In addition, though aluminum borohydride and beryllium borohydride are generally not regarded as shock-sensitive, there is little experimental evidence on this point since these materials are so difficult to handle in the test apparatus normally employed for such determinations.

In accordance with the instant invention, it has been discovered that the reaction of a metal borohydride, i.e., aluminum borohydride, beryllium borohydride, or zirconium borohydride, with a ligand composed solely of carbon, hydrogen, etheric oxygen, and amino nitrogen atoms, results in novel adducts which have exceptional and valuable utility in various fields of application. These novel adducts, as the fuel component in a propellant system, possess a combination of well balanced properties, especially the novel liquid adducts when employed as hypergolic fuels. The novel solid adducts can be used as energetic additives in solid propellants. The novel adducts, also, are useful as additives in fuels for conventional air-breathing engines whereby the combustion and flame-out characteristics of the hydrocarbon jet fuels are improved. The novel adducts have further utility as additives to liquid hydrocarbon rocket fuels in bipropellant rocket engines employing oxidizers such as liquid oxygen or nitrogen tetroxide wherein the presence of said novel

adducts improves the combustion characteristics of said propellant systems as, for example, by preventing combustion instability or resonant burning.

In addition, the physical properties of the novel adducts are dramatically more desirable than the corresponding metal borohydride per se. For example, the novel adducts are more stable, and less hazardous than the parent metal borohydride. In general, the densities of the aluminum borohydride adducts are markedly higher than the density of aluminum borohydride.

Accordingly, one or more objects will be achieved by the practice of the invention.

It is an object of the invention to provide novel adducts of various metal borohydrides with ligands composed solely of carbon, hydrogen, etheric oxygen, and amino nitrogen atoms. Another object of the invention is directed to providing novel processes for preparing the aforementioned adducts. A further object of the invention is directed to the preparation of novel high energy fuels of well balanced properties for use in propellant systems. A still further object of the invention is directed to novel adducts which are useful as additives in conventional fuels, e.g., jet fuels for airbreathing engines, and hydrocarbon fuels for use in liquid bipropellant rocket motors, to thus improve the combustion characteristics and the hyperglocity of said fuels. Another object of the invention is to provide novel adducts which are useful as fuels for the generation of a driving fluid for power turbines such as auxiliary power turbines in spacecraft or underwater propulsion systems utilizing, for example, sea water as an oxidizer component. Other objects of the invention are directed to the preparation of novel adducts having utility as reducing agents, stabilizers, color improvers, etc., which are useful in various fields of application such as in the refining of organic liquids, synthetic resins, and the like. These and other objects will become apparent to those skilled in the art from a consideration of the instant specification.

The broad aspect of the invention encompasses novel adducts of aluminum borohydride, beryllium borohydride, or zirconium borohydride with a ligand composed solely of carbon, hydrogen, etheric oxygen, and amino nitrogen atoms. The ligands which are contemplated as a reagent in the preparation of the novel adducts are further characterized in that they contain at least one etheric oxygen atom and/or amino nitrogen atom which functions as a Lewis base. In accordance with the Werner coordination theory, the resulting novel adducts, from a structural interpretation, can be characterized as containing at least one amino nitrogen to metal coordinate bond and/or at least one etheric oxygen to metal coordinate bond. It should be noted that of all the amino nitrogen atoms and etheric oxygen atoms of the ligand which can function as a Lewis base, at least one of said amino nitrogen atoms and/or etheric oxygen atoms is coordinately bonded to a metal atom (of the metal borohydride). In addition, the metal atom (of the metal borohydride) can be coordinately bonded to more than one amino nitrogen atom and/or etheric oxygen atom which functions as a Lewis base. However, as indicated previously, the ligand must contain at least one amino nitrogen atom and/or etheric oxygen atom which functions as a Lewis base. It is preferred that the ligand contain up to 6 amino nitrogen atoms, and up to 6 etheric oxygen atoms in the molecule, and more preferably, up to 4 amino nitrogen atoms and up to 4 etheric oxygen atoms in the molecule. It is preferred, also, that any hydrocarbon substituents which are monovalently bonded to the amino nitrogen atoms and/or etheric oxygen atoms contain up to 12 carbon atoms, and preferably still, up to 3 carbon atoms. Hydrogen and

methyl substituents on the amino nitrogen atoms are highly preferred.

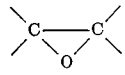
The term "etheric oxygen atom(s)," as used herein including the appended claims, is employed to designate those oxygen atoms which have the structure —O— and which can be positioned in an aliphatic or a cyclic moiety of the molecule. Moreover, the term "etheric oxygen atom(s)" excludes those oxygen atoms in the form of ester groups, i.e.,



carbonyl groups, i.e.,



hydroxy groups, i.e., —OH; and vicinalepoxy groups, i.e.,



It is further pointed out that the word "adduct(s)," as used herein including the appended claims is employed in its broadest sense and encompasses within its scope complexes, coordination compounds, chelates, and the like.

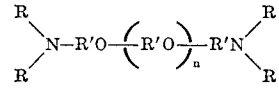
In one aspect, the invention encompasses novel adducts of metal borohydrides with a ligand composed solely of carbon, hydrogen, etheric oxygen, and amino nitrogen atoms in which at least one etheric oxygen atom and/or amino nitrogen atom functions as a Lewis base. In another aspect, the ligand is composed solely of carbon, hydrogen, etheric oxygen, and amino nitrogen atoms in which at least one etheric oxygen atom and/or amino nitrogen atom is bonded to another amino nitrogen atom. In still another aspect, the ligand is composed solely of carbon, hydrogen, etheric oxygen, and amino nitrogen atoms in which at least one etheric oxygen atom and/or amino nitrogen atom functions as a Lewis base, and in which the amino nitrogen atoms are present in the form of secondary amino groups and/or tertiary amino groups.

In a particularly preferred aspect, the novel adducts of the invention can be represented by the following formula:

$$\text{I} \qquad L\cdot[M(BH_4)_x]_n$$

wherein L is a ligand composed solely of carbon, hydrogen, etheric oxygen, and amino nitrogen atoms in which at least one etheric oxygen atom and/or amino nitrogen atom functions as a Lewis base; wherein M represents aluminum, beryllium, or zirconium; wherein x is the valence of M; and wherein n is an integer having a minimum value of one and a maximum value no greater than the total number of etheric oxygen atoms and amino nitrogen atoms contained in the ligand (L) which function as Lewis bases. Consequently, the maximum value of n will be determined by the number of etheric oxygen and amino nitrogen to metal coordinate bonds present in the novel adduct. This in turn will be governed by the choice of the ligand and, in general, by the proportions of the reagents, i.e., ligand and metal borohydride, which are employed in the preparation of the novel adducts. For example, the ligand 2,2'-bis(3-aminopropoxyethyl) ether has two amino nitrogen atoms and three etheric oxygen atoms which can function as Lewis bases. Equimolar ratios of aluminum borohydride and this compound will react to yield a white solid adduct. On the other hand, a ration of five moles, or more, of aluminum borohydride per mole of this ligand yields a clear liquid adduct. Any aluminum borohydride in excess of the 5 to 1 molar ratio can be recovered as unreacted reagent. Thus, in the light of the preceding illustrations (as well as the operative examples in the specification), it is readily apparent that the number of etheric oxygen atoms and amino nitrogen atoms which are capable of functioning as Lewis bases realistically governs the maximum value of the variable n in Formula I supra. It is preferred that n be an integer having a value greater than zero and less than 8, and preferably still, greater than 1 and less than 6.

Illustrative ligands which are contemplated in the preparation of the novel adducts include, among others, the mono-, di-, and tri(hydrocarbyloxy)amines, e.g., methoxyamine, dimethoxyamine, trimethoxyamine, ethoxyamine, diethoxyamine, triethoxyamine, propoxyamine, dipropoxyamine, tripropoxyamine, butoxyamine, dibutoxyamine, tributoxyamine, dihexoxyamine, tridodecoxyamine, trioctadecoxyamine, dicyclopentoxyamine, tricyclohexoxyamine, cycloheptoxyamine, diphenoxyamine, di(alkylphenoxy)amine, tritoloxyamine, tri(phenethoxy)amine; the mono- and poly(hydrocarbyloxy)diaminoalkanes, e.g., the N-methoxy-, N,N-dimethoxy-, N,N,N'-trimethoxy-, and N,N,N',N' - tetramethoxy-1,2-diaminoethanes, the N - ethoxy-, N,N - diethoxy-, N,N,N'-triethoxy-, and N,N,N',N'-tetraethoxy - 1,3 - diaminopropanes, the N-propoxy-, N,N-dipropoxy-, N,N,N'-tripropoxy-, and N,N,N',N'-tetrapropoxy-1,4-diamino-butanes, the N-methoxy-, N,N-dimethoxy-, N,N,N'-trimethoxy-, and N,N,N',N'-tetramethoxy - 1,6 - diaminohexanes, N-cyclohexoxy-1,3-diaminopropane, N,N'-diphenoxy - 1,4-diaminobutane, N,N,N',N' - tetraphenethoxy - 1,6 - diaminopentane, N,N,N',N' - tetratoloxy - 1,3-diaminopropane, and the like; the mono- and poly(hydrocarbyloxy) substituted polyalkylenepolyamines wherein the hydrocarbyloxy radical is monovalently bonded to the same or different amino nitrogen atoms and can represent methoxy, ethoxy, propoxy, butoxy, hexoxy, octoxy, decoxy, dodecoxy, octadecoxy, cyclopentoxy, cyclohexoxy, cycloheptoxy, phenoxy, toloxy, phenethoxy, phenylpropoxy, etc., and wherein the polyalkylenepolyamine moiety can represent diethylenetriamine, triethylenetetramine, tetraethylenepentamine, pentaethylenehexamine, the polypropylenepolyamines, the polybutylenepolyamines, the polyethylenepolypropylenepolyamines, hexamethylenetetramine, and the like; the polyetherdiamines having the formula



wherein each R can be hydrogen, alkyl, or alkoxy, preferably hydrogen, lower alkyl, or lower alkoxy, wherein each R' is a divalent saturated aliphatic hydrocarbon preferably containing from 1 to 4 carbon atoms, and preferably still, methylene, wherein n is an integer having a value of at least one, and preferably a value from 1 to 6, e.g., the bis(aminoalkoxyalkyl)ethers such as 2,2' - bis(3-aminopropoxyethyl)ether, 2,2'-bis(2-aminoethoxyethyl)-ether, 2,2' - (4-aminobutoxyethyl)ether, 2,2' - (5-aminopentoxypropyl)ether and the like; the mono- and poly(hydrocarbyloxy) substituted heterocyclic compounds which contain at least one nitrogen atom in the heterocyclic nucleus, e.g., 4-methoxypyridine, 4-ethoxypyridine, 3-n-butoxypyridine, 3-hexoxypyridine, 4 - methoxypiperidine, 4-ethoxypiperidine, 2-isobutoxypiperidine, 3-methoxypyrrole, 3-propoxypyrrole, 2 - methoxyquinoline, 3-hexoxyquinoline, and the like; the mono- and poly(hydrocarbyloxy)anilines, e.g., 4-methoxyaniline, 2-ethoxyaniline, 4-pentoxyaniline, and the like.

Other ligands which are contemplated include morpholine, the lower alkylmorpholines, the oxazoles, the oxadiazoles, the oxatriazoles, the dioxazoles, the oxazines, the oxadiazines, the lower alkoxycarbazoles, methoxyhydrazine, unsymmetrical dimethoxyhydrazines, and the like.

The hydrocarbyloxy substituted amines, the hydrocarbyloxy substituted diaminoalkanes, the hydrocarbyloxy substituted polyalkylenepolyamines, the polyetherdiamines, the hydrocarbyloxy substituted heterocyclic compounds, etc., which are illustrated supra, also can con-

tain hydrocarbyl substituents, e.g., alkyl, cycloalkyl, aryl, etc., preferably alkyl substituents which have from 1 to 4 carbon atoms.

It is pointed out that by the term "hydrocarbyloxy," as used herein including the appended claims is meant the monovalent radical, RO—, where R is composed of carmonovalent radical, RO—, wherein R is composed of carbon and hydrogen, and is free of ethylenic and acetylenic unsaturation. Illustrative hydrocarbyloxy radicals include alkoxy, cycloalkoxy, cycloalkylalkoxy, aryloxy, arylalkoxy, and alkaryloxy. The limitation "lower" before the word alkyl or alkoxy, as used herein including the appended claims, restricts the alkyl and alkoxy radicals to those containing from 1 to 6 carbon atoms.

Illustrative novel adducts which are encompassed within the scope of the invention include, among others, the adducts of aluminum borohydride with morpholine, aluminum borohydride with 2 - methylmorpholine, aluminum borohydride with 2,2′ - bis(3-aminopropoxyethyl)-ether, aluminum borohydride with 2,2′-bis(2-aminoethoxyethyl) ether, aluminum borohydride with 2,2′ - bis(3-aminopropoxypropyl) ether, aluminum borohydride with dimethoxyamine, aluminum borohydride with dimethoxyamine, aluminum borohydride with trimethoxyamine, aluminum borohydride with triethoxyamine, aluminum borohydride with 4-methoxyaniline, aluminum borohydride with 4-methoxypyridine, aluminum borohydride with 4-methoxypiperidine, beryllium borohydride with morpholine, beryllium borohydride with 2-methylmorpholine, beryllium borohydride with 2,2′-bis(3-aminopropoxyethyl) ether, beryllium borohydride with 2,2′-bis(3-aminoethoxyethyl) ether, beryllium borohydride with 2,2′-bis(3-aminopropoxypropyl) ether, beryllium borohydride with methoxyamine, beryllium borohydride with dimethoxyamine, beryllium borohydride with trimethoxyamine, beryllium borohydride with ethoxyamine, beryllium borohydride with triethoxyamine, beryllium borohydride with 4-methoxyaniline, beryllium borohydride with 4-methoxypyridine, beryllium borohydride with 4-methoxypiperidine, zirconium borohydride with morpholine, zirconium borohydride with 2,2′ - bis(3-aminopropoxyethyl) ether, zirconium borohydride with 2,2′ - bis(2-aminoethoxyethyl) ether, zirconium borohydride with 2,2′ - bis(3 - aminopropoxypropyl) ether, zirconium borohydride with methoxyamine, zirconium borohydride with trimethoxyamine, zirconium borohydride with 4-methoxyaniline, zirconium borohydride with 4-methoxypiperidine, and the like.

The novel adducts can be prepared by contacting the metal borohydride with the ligand under an inert, anhydrous atmosphere, e.g., hydrogen, nitrogen, argon, helium, krypton, and the like. If desired, an inert normally-liquid, organic vehicle, described hereinafter, can be employed. It is essential that impurities such as oxygen, carbon dioxide, carbon monoxide, water, and other materials which are reactive with metal borohydride be avoided in the system in view of the highly hazardous and explosive nature of the borohydride reagent. The operative temperature can be in the range of from about —64° C., and lower, to below the boiling point of aluminum borohydride, e.g., from about —64° C. to 43° C. A preferred temperature range is from about 0° C. to about 30° C., and preferably still, from about 15° C. to about 25° C. The order of addition of the reagents does not appear to be narrowly critical. However, it is preferred that the metal borohydride, preferably contained in an inert normally-liquid organic vehicle, be added to the ligand. Incremental isothermal addition of the metal borohydride to the ligand, with slow stirring, is highly preferred. If desired, the reaction mixture can be cooled to maintain the desired reaction temperature. The operative pressure can be subatomospheric, atmospheric, or moderately superatmospheric. In general, suitable results have been obtained by conducting the reaction below about 760 mm. of Hg pressure. It is preferred that the operative pressure be in the range of from about 10^{-3} mm. of Hg to about 760 mm. of Hg. For relatively large batch production of the novel adducts, it was observed that satisfactory results were obtained by effecting the reaction under essentially atmospheric pressure.

In view of the hazardous nature of the metal borohydride, it is not preferred to have a large excess of unreacted metal borohydride present in the reaction product mixture. In the preparation of the novel liquid adducts, the preferred maximum concentration of metal borohydride is in slight excess of the quantity which is necessary to react with the ligand to produce the desired liquid adduct. On the other hand, when employing relatively high boiling ligands to prepare the novel liquid adducts, the presence of unreacted ligand in the resulting reaction product mixture is undesirable since the resolution of said mixture, by distillation, could result in the thermal decomposition of the liquid adduct product. However, this disadvantage does not present itself when the resulting product is a solid adduct. In such cases, the solid adduct, if insoluble in the reaction product mixture, is readily recovered therefrom via filtration techniques. Should the solid adduct be soluble in the reaction product mixture, the addition of an inert, normally-liquid, organic vehicle thereto in which the solid adduct product is insoluble and the relatively high boiling ligand is miscible, would result in the precipitation of said solid adduct. The solid adduct then could be recovered by filtration procedures, as indicated previously. Subject to the variables illustrated above, it is desirable to employ an amount of metal borohydride which is slightly in excess of that required to react with the total amount of ligand to produce the desired novel liquid adduct, whereas it is desirable to employ an amount of ligand which is moderately in excess of that required to react with the total amount of metal borohydride to produce the desired novel solid adducts. However, it is preferred to employ essentially stoichiometric amounts of the reagents.

The reaction period will depend, to a significant extent, upon various factors such as the choice of the ligand and metal borohydride, the concentration of the reactants, the operative temperature, the operative pressure, the manner of addition of the reactants, the use of an inert, normally-liquid, organic vehicle, and other considerations. Depending upon the correlation of the variables illustrated supra, the reaction period can range from several minutes to a few days. However, highly satisfactory results have been obtained by conducting the reaction over a period of from about 0.5 hour, and lower, to about 6 hours, and higher.

If desired, the reaction can be effected in the presence of an inert normally-liquid, organic vehicle, i.e., a vehicle which is non-reactive with the reagents or the resulting novel adduct product. Illustrative vehicles include, for example, the normally-liquid saturated aliphatic and cycloaliphatic hydrocarbons, e.g., n-pentane, n-hexane, n-heptane, iso-octane, n-octane, cyclopentane, cyclohexane, cycloheptane, methylcyclohexane, ethylcyclopentane, and the like; the aromatic hydrocarbons, e.g., benzene, toluene, xylene, ethylbenzene, and the like; and other inert, normally-liquid, organic vehicles which would become readily apparent to one skilled in the art. The use of an inert vehicle permits the heat of reaction to be more evenly dispersed, thus minimizing the danger of inadvertently causing thermal decomposition of unreacted metal borohydride. This advantage is especially desirable when employing large quantities of reagents.

The novel adduct product can be recovered from the reaction product mixture by various procedures known to the art. For example, excess reagent and inert vehicle, if any, can be recovered from the reaction product mixture by distillation under reduced pressure, e.g., 10 to 50 mm. of Hg. The novel solid adducts also can be recovered from the reaction product mixture by filtration or crystallization techniques. Vacuum distillation is a preferred method of recovering the novel adduct product

providing it can be vacuum distilled without decomposition.

The preparation of aluminum borohydride,[1] beryllium borohydride,[2] and zirconium borohydride [3] is documented in the literature.

A preferred embodiment of the invention is directed to the preparation of novel liquid propellant systems which utilize the novel liquid adduct as the fuel component. Many of the novel liquid adducts are highly attractive in that they are capable of giving a high specific impulse with appropriate oxidizers when used as liquid fuels in liquid propellant systems. As is well known, the specific impulse is a measure of the pounds of thrust obtainable per pound of propellant (fuel+oxidizer) reacted per second. A higher specific impulse makes possible an increased range or trajectory of a vehicle driven by jet propulsion, or an increased payload, or a decreased fuel requirement, or a higher velocity at burnout.

Examples of appropriate liquid oxidizers, both storable and cryogenic include nitrogen tetroxide, the fuming nitric acids, chlorine trifluoride, hydrogen peroxide, bromine pentafluoride, oxygen, fluorine, oxygen difluoride, perchloryl fluoride, perfluoroguanidine, and others. The ratio of oxidizer to novel fuel is generally chosen so as to maximize the specific impulse delivered by the given propellant system, except when said propellant system is employed in a gas generator to furnish hot compressed, driving fluid to power a turbine. When used for gas generation, it is generally advantageous to employ a fuel-rich ratio so as to limit the temperature of the combustion products in order to avoid heat damage to the turbine. Another important advantage of various novel liquid adducts is their ability to form hypergolic propellant systems with certain liquid oxidizers that normally do not effect hypergolic combustion with common rocket fuels. Hypergolic combustion is particularly important in spacecraft propulsion which may require intermittent combustion and variable thrust capabilities.

Another preferred embodiment of the invention is directed to the preparation of novel solid propellant formulations which utilize the novel solid adducts as a fuel component. Solid rocket propellants can be termed monopropellants in that a solid oxidizer and solid fuel are mixed together in a single matrix which does not require the addition of oxidizer from an external source. An important class of solid propellant systems are known as composite solid propellants which can be prepared by suspending a solid oxidizing agent in a liquid prepolymer which is capable of being cast and cured to a combustible elastomeric matrix. Composite solid propellants can be made in a great variety of compositions. Various constituents can be added to modify the characteristics of the propellant such as to improve the energetics, to improve the physical properties, to catalyze or retard the burning process, and the like. Oxidizers which can be employed include, for example, ammonium perchlorate, ammonium nitrate, nitronium perchlorate, hydrazine nitrate, hydrazine perchlorate, quanidinium perchlorate, and others. Exemplary binders include polyethylene, the butadiene-acrylic acid copolymers, the polyether polyurethanes, the fluorocarbons, and other elastomeric binders. A typical standard solid propellant composition can contain about 65 weight percent ammonium perchlorate, 15 weight percent polymeric hydrocarbon binder, and 20 weight percent aluminum powder which would produce upon combustion (at 1,000 p.s.i.) a theoretical specific impulse of about 265 pounds-second/pound. However, the actual delivered specific impulse has been somewhat less. To improve the performance of such solid propellant systems, the subject embodiment contemplates the use of the novel solid adducts as a high energy solid fuel additive to replace part or all of the less energetic fuel additives, such as aluminum, now commonly used. As is readily apparent to those skilled in the art, the quantity and choice of the novel solid adduct to be incorporated to form the novel solid propellant in order to achieve well balanced properties and optimum performance will be governed by various factors such as the compatibility with the chosen binder, the thermal stability of the novel adduct, the oxidizer of choice, the nature and concentration of burning rate modifiers, and other considerations. In a preferred aspect, the novel solid adduct is encapsulated within a combustible material such as, for example, polyethylene, polypropylene, aluminum, polytetrafluoroethylene, polyalkyl siloxanes, and the like. The art is well-apprised of the technique of encapsulating a solid fuel component which is to be incorporated in a solid propellant.

Another preferred embodiment of the invention relates to novel compositions of liquid fuels which contain the novel adduct in an amount sufficient to improve the combustion characteristics, ignition efficiency, flame stability, and/or energetics of said liquid fuel. The liquid fuels which are contemplated are useful as fuels for jet propulsion purposes which include, among others, air-breathing engines and liquid rocket engines, e.g., turbojets, ramjets, bipropellant rockets, and other combustion power plants. Although a maximum increase in specific impulse is produced by using a maximum quantity of the novel adduct, other practical considerations connected with the particular applications of the fuel often lead to preferred mixtures containing less than the maximum compatible quantity of novel adduct. The attainment of well balanced properties in the novel liquid fuels is governed by many of the variables discussed previously, e.g., choice of liquid fuel, the choice of the novel adduct solubility, specific application of the novel liquid fuel, the addition of modifying components, hypergolicity, and economic factors. Illustrative liquid fuels include the aliphatic, hydroaromatic, and aromatic hydrocarbons, and mixtures thereof, for example, kerosene (RP–1, JP–4, JP–5, JP–6), n-hexane, diethylcyclohexane, petroleum ether (boiling range 30°–60° C.), benzene, toluene, xylene, and the like; aliphatic, aromatic, and heterocyclic amines such as isopropylamine, diethylamine, aniline, cyclohexylamine, pyridine, and the like; cyclic ethers such as dioxane, furan, tetrahydrofuran; and others.

Additional embodiments which are contemplated within the scope of the invention involve the use of the novel adducts as color improvers, as stabilizers, as reducing agents, as antioxidants, as redox catalysts, as catalysts for olefin polymerization processes, and so forth. Contaminants such as carbonyl compounds in oxygenated organic compounds, e.g., Oxo alcohols, are readily reduced by incorporating a small quantity of the novel adduct thereto. Of course, contaminated oxygenated organic compounds such as aldehydic compounds that can react with the novel adduct are not applicable. The amount of novel adduct which can be added, in general, is approximately sufficient to react with the contained contaminants. Oxidative degradation which results from traces of oxygen or oxygen-containing compounds contained in, for example, synthetic polymers, can be prevented by incorporating into said polymers an antioxidant amount of the novel adduct. The novel adducts can be employed as catalysts for the polymerization of olefins, ethylene, propylene, the butylenes, styrene, etc., preferably via the so-called low pressure techniques. The optimum catalyst concentration is readily apparent to those skilled in the art.

As is well known, the heat of formation of a compound can be defined as the enthalpy change upon forming said compound from its elements in their standard state. The heats of formation of the ligands and the metal borohydrides were calculated from standard heats of

[1] U.S. Patent No. 2,599,203.
[2] Berg et al., J. Am. Chem. Soc., 62, 3425 (1950).
[3] U.S. Patent No. 2,575,760.

combustion which, in turn, were determined experimentally or by using the Handrick [4] group contribution method.

It is pointed out that the terms "chamber pressure" and "exhaust pressure," as used herein, are standardized at 1,000 p.s.i.a. and 14.7 p.s.i.a., respectively. Once these terms are specified at the above said pressures, the theoretical shifting specific impulse is a thermodynamically defined quantity that depends on the fuel composition and heat of formation, the oxidizer composition and heat of formation, and the oxidizer to fuel ratio. The specific impulse data presented herein were determined by making performance calculations at selected oxidant to fuel ratios, and then plotting the results to define the maximum specific impulse and the optimum oxidant to fuel ratio. In general, the calculations were performed on an IBM 7090 computer using a chemical equilibrium program prepared by the U.S. Naval Ordnance Test Station [5] together with thermodynamic data for combustion species supplied with the program. In a few instances, the performance curves were extrapolated to low oxidant to fuel ratios by computing additional relative specific impulse values by the approximate NARTS hand calculation method,[6] with thermodynamic data for combustion products supplied with the method.

By the term "energetics," as used herein, is meant the chemical energy release upon combustion, or, more particularly, the theoretical specific impulse.

The following examples are illustrative.

EXAMPLE 1

(A) Morpholine, 0.370 gram, 4.25 mmoles, was transferred by means of a hypodermic needle under a dry nitrogen atmosphere into a reaction flask equipped with a standard taper joint and a Teflon coated magnetic stirring bar. The reaction flask then was attached to a high vacuum system, cooled with a liquid nitrogen bath, and evacuated to at least 10^{-3} mm. of mercury. Aluminum borohydride, 4.36 mmoles, was measured in a standard bulb and subsequently added in increments to said morphine. After each addition, the liquid nitrogen bath was removed and the reaction flask allowed to warm to room temperature and stirring was initiated. The pressure changes during the reaction were observed with a mercury monometer attached to the system. When pressure changes were no longer observed, the reaction flask was cooled with liquid nitrogen and any non-condensable gas collected in a Toepler pump. The results are summarized in Table I infra.

TABLE 1.—PRESSURE-COMPOSITION DATA FOR THE REACTION OF ALUMINUM BOROHYDRIDE WITH MORPHOLINE AT 25° C.

$Al(BH_4)_3$ Added, cumulative Mmoles	Mole ratio, $Al(BH_4)_3$/ morpholine	Total pressure, mm. of Hg	Remarks
1.35	0.318	4.5	1.37 mmoles of H_2 evolved. Product all white solids.
3.51	0.826	3.3	No N_2 evolved. More white solids.
4.36	1.03	31	No H_2 evolved. Pressure decreasing very slowly. Product all white solids.

The results indicate that the pressure remains relatively low until a mole ratio of aluminum borohydride to morpholine exceeds one, signifying that one mole of aluminum borohydride had reacted with morpholine in a 1:1 ratio to produce the white solid addition compound, morpholine aluminum borohydride. The relatively small quantity of hydrogen released after the first addition of aluminum borohydride can be attributed to the presence of impurities or side reactions. No hydrogen was evolved upon subsequent additions of aluminum borohydride. A small quantity of the gas was distilled from the reaction flask at room temperature, whereupon the pressure above the solid was less than 2 mm. of Hg. The vapor pressure of the gas removed indicated that it was aluminum borohydride. The presence of any unreacted morpholine was not detected.

Dry benzene, 4.0 ml., was transferred into another reaction system of the same volume as that used for the morpholine reaction. The vapor pressure was 115 mm. of Hg at 27.0° C. Aluminum borohydride, 4.14 mmoles, was added to the benzene and the vapor pressure of the mixture was found to be 42.5 mm. of Hg at 27.0° C. This mixture of benzene and aluminum borohydride was then distilled at room temperature onto the morpholine-monoaluminum borohydride adduct and allowed to react for several hours. No precipitate was present in the resulting mixture.

All of the readily distillable material was then removed from the reaction flask. The vapor pressure of this liquid was 115 mm. of Hg at 27.0° C., indicating that it was benzene. Hence, the aluminum borohydride had reacted with morpholine-monoaluminum borohydride. A total of 8.50 mmoles of aluminum borohydride had reacted with 4.25 mmoles of morpholine to form a non-volatile, white solid morpholine-dialuminum borohydride adduct.

(B) In an analogous manner as part A above, when beryllium borohydride is employed in lieu of aluminum borohydride, there is obtained a beryllium borohydride adduct of morpholine.

(C) In an analogous manner as part A above, when triethoxyamine is employed in lieu of morpholine, there is obtained an aluminum borohydride adduct of triethoxyamine.

EXAMPLE 2

(A) 2,2'-bis(3-aminopropoxyethyl) ether, 0.104 gram, 0.471 mmole, and five milliliters of dry benzene, were transferred into a reaction flask and reacted incrementally with aluminum borohydride in the manner described in Example 1. The data are summarized in Table II infra.

TABLE II.—PRESSURE COMPOSITION DATA FOR THE REACTION OF ALUMINUM BOROHYDRIDE WITH 2,2'-BIS (3-AMINOPROPOXYETHYL) EITHER IN BENZENE AT 25° C.

$Al(BH_4)_3$ Added, cumulative mmoles	Mole ratio, $Al(BH_4)_3$/ gycol	Total pressure, mm. of Hg	Remarks
0.472	1.00	115	White solid noted. Only a trace of H_2 evolved.
1.02	2.17	115	More solids appearing. Trace of H_2 evolved.
1.60	3.40	115	Solids still present.
1.93	4.11	115	Solids present.
2.34	4.99	115	Solution clear.

The above results show that the total pressure of the benzene mixtures remained constant throughout all of the aluminum borohydride additions. If the aluminum borohydride had not reacted, the pressure over the benzene solutions would have increased. It was, therefore, concluded that aluminum borohydride reacted with the ligand up to ratios of five moles of borohydride to one of the ligand. When a mole ratio of 4:1 had been reached the product was, at least in part, composed of solids. The 5:1 composition was composed of a viscous, relatively non-volatile liquid after benzene was distilled from the mixture at room temperature. Essentially no hydrogen was evolved during the entire experiment. Example 2A established the preparation of five adducts of aluminum borohydride with the ether reagent, that is, the 2,2'-bis-(3-aminopropoxyethyl) ether adducts of mono-, di-, tri-, tetra-, and pentaaluminum borohydride.

[4] G. R. Handrick, Ind. and Eng. Chem. 48, No. 8, page 1366, August 1956.

[5] "The Theoretical Computation of Equilibrium Compositions, Thermodynamic Properties and Performance Characteristics of Propellant Systems," NAVWEPS Report 7043, June 8, 1960.

[6] J. D. Clark, The "NQD" Method of I_{sp} Calculation, Letter Report L-23, Naval Air Rocket Test Station, Lake Denmark, N.J., September 1959.

(B) In an analogous manner as part A above, when beryllium borohydride is employed in lieu of aluminum borohydride, there is obtained the beryllium borohydride adducts of 2,2'-bis(3-aminopropoxyethyl) ether.

(C) In an analogous manner as part A above, when 2,2'-bis(2-aminoethoxypropyl) ether is employed in lieu of 2,2'-bis(3-aminopropoxyethyl) ether, there is obtained the aluminum borohydride adducts of 2,2'-bis(2-aminoethoxypropyl) ether.

EXAMPLE 3

(A) Tensimetrically pure methoxyamine, 0.676 mmole, measured as a gas, was transferred into a 25 ml. reaction flask as described in Example 1. Aluminum borohydride was then added in increments and the pressure-composition data for the experiment recorded. They are summarized in Table III infra.

TABPE III.—PRESSURE-COMPOSITION DATA FOR THE REACTION OF ALUMINUM BOROHYDRIDE WITH METHOXYAMINE AT 25° C.

$Al(BH_4)_3$ added, cumulative mmoles	Mole ratio, $Al(BH_4)_3/CH_3ONH_2$	Total pressure, mm. of Hg	H_2 evolved, cumulative mmoles	Remarks
0.214	0.317	8	Trace	Product composed entirely of white solids.
0.595	0.880	10	0.18	Product contains white solid.
0.778	1.15	48	0.42	Product liquid with some solids.
1.84	2.74	155	0.75	Product liquid after removal of excess aluminum borohydride.

These data indicate that the pressure remained relatively low and constant until the mole ratio of aluminum borohydride to amine was one. At a greater ratio of aluminum borohydride, the vapor pressure increased sharply; it was concluded, therefore, that aluminum borohydride reacted with methoxyamine in a mole ratio of one to one, approximately one mole (0.75/0.68=1.1) of a non-condensable gas, presumably hydrogen, was formed per mole of amine used.

The excess vapors were distilled from the reaction flask at room temperature and found to be aluminum borohydride, identified by its vapor pressure

(V.P.=120 mm. of Hg at 0° C.)

The product was a clear, non-volatile liquid.

(B) In an analogous manner as part A above, when beryllium borohydride and N,N,N',N'-tetramethoxy-1,3-diaminopropane are employed in lieu of aluminum borohydride and methoxyamine, respectively, there is obtained the beryllium borohydride adducts of N,N,N',N'-tetramethoxy-1,3-diaminopropane.

(C) In an analogous manner as part A above, when N-methyl-N-methoxyamine is employed in lieu of methoxyamine, there is obtained the aluminum borohydride adduct of N-methyl-N-methoxyamine.

EXAMPLES 4–13

In the following examples, the theoretical performance of various novel liquid adducts oxidized with nitrogen tetroxide is calculated. The specific impulse values (pound-second/pound) of these novel liquid propellant systems are compared with three standard liquid propellant systems (also oxidized with nitrogen tetroxide). The data are set forth in Table IV infra.

TABLE IV

Ex. No.	Fuel	$\Delta H_f°$, Kcal/mole [3]	Specific impulse (I_{sp}) [4]	Density impulse ($I_{sp}d$) [6]
4	Hydrazine [1]	+12.05	291	357
5	Unsymmetrical dimethylhydrazine (UDMH) [1]	+12.72	285	----------
6	50 wt. percent hydrazine +50 wt. percent UDMH. [2]	[5] +29.38	288	----------
7	Methoxyamine aluminum borohydride.	17.90	322	383
8	Methoxyamine beryllium borohydride.	14.00	344	----------
9	Methoxyamine zirconium borohydride.	−21.10	299	>864
10	N-methyl-N-methoxyamine aluminum borohydride.	−3.30	316	----------
11	2,2'-bis(3-aminopropoxyethyl) ether pentaaluminum borohydride.	−78.7	311	390
12	2,2'-bis(3-aminopropoxyethyl) ether pentaberyllium borohydride.	−98.2	321	----------
13	2,2'-bis(3-aminopropoxyethyl) ether pentazirconium borohydride.	−184.2	289	805

[1] Standard liquid fuel for comparison.
[2] Standard liquid fuel for comparison. Said liquid propellant system has been designated for the Titan ICBM.
[3] Heat of formation.
[4] Maximum theoretical performance with N_2O_4 at 1,000 p.s.i. expanded to 14.7 p.s.i., shifting equilibrium, I_{sp} (lb./sec.-lb.).
[5] Kcal./100 grams.
[6] Theoretical maximum density impulse with N_2O_4 at 1,000 p.s.i. expanded to 14.7 p.s.i., shifting equilibrium, $I_{sp}d$ (sec.) (g./cc.).

EXAMPLES 14–17

In the following examples, the theoretical performance of various novel solid adducts oxidized with ammonium perchlorate is calculated. The specific impulse values (pound-second/pound) of these novel solid propellant systems are compared with a standard solid propellant system (also oxidized with ammonium perchlorate). The theoretical performance calculations are based on the solid fuel plus oxidizer plus 20 weight percent of a standard hydrocarbon binder. The data are set forth in Table V infra.

TABLE V

Ex. No.	Fuel	Concentration of fuel [1]	$\Delta H_f°$, Kcal./mole [2]	Specific impulse (I_{sp}) [3]
14	Aluminum [4]		0.0	263
15	Morpholine dialuminum borohydride		−18.3	275
16	Morpholine diberyllium borohydride		−26.1	(280-285)
17	Morpholine dizirconium borohydride		−96.3	(260-265)

[1] Weight percent of fuel.
[2] Heat of formation.
[3] Maximum theoretical performance with NH_4ClO_4 at 1,000 p.s.i. expanded to 14.7 p.s.i., shifting equilibrium.
[4] Standard solid fuel for comparison.

What is claimed is:

1. An adduct of a metal borohydride of the group consisting of aluminum borohydride, beryllium borohydride, and zirconium borohydride, with a ligand composed solely of carbon, hydrogen, etheric oxygen, and amino nitrogen atoms, wherein at least one of said atoms of the group consisting of etheric oxygen and amino nitrogen atoms functions as a Lewis base, and wherein said adduct possesses at least one coordinate bond between the metal moiety of said metal borohydride and an atom of the group consisting of etheric oxygen and amino nitrogen atoms of said ligand.

2. The adduct of claim **1** wherein said metal borohydride is aluminum borohydride.

3. An adduct of a metal borohydride of the group consisting of aluminum borohydride, beryllium borohydride, and zirconium borohydride, with a ligand composed solely of carbon, hydrogen, etheric oxygen, and amino nitrogen atoms, wherein at least one etheric oxygen atom functions as a Lewis base, and wherein said adduct possesses at least one coordinate bond between the metal moiety of said metal borohydride and an etheric oxygen atom of said ligand.

4. An adduct of a metal borohydride of the group consisting of aluminum borohydride, beryllium borohydride, and zirconium borohydride, with a ligand composed solely of carbon, hydrogen, etheric oxygen, and amino nitrogen atoms, wherein at least one amino nitrogen atom functions as a Lewis base, and wherein said adduct possesses at least one coordinate bond between the metal moiety of said metal borohydride and an amino nitrogen atom of said ligand.

5. An adduct having the following formula

$$L\cdot[M(BH_4)_x]_n$$

wherein L is a ligand composed solely of carbon, hydrogen, etheric oxygen, and amino nitrogen atoms with the proviso that at least one of the atoms of the group consisting of etheric oxygen and amino nitrogen atoms functions as a Lewis base, wherein M is of the group consisting of aluminum, beryllium, and zirconium, wherein x is the valence of M, and wherein n is an integer having a minimum value of one and a maximum value equal to the number of etheric oxygen and amino nitrogen atoms which function as Lewis bases.

6. The adduct of claim **5** wherein M is aluminum borohydride.

7. An adduct of aluminum borohyride with morpholine, said adduct possessing at least one coordinate bond between the aluminum moiety of said aluminum borohydride and an atom of the group consisting of etheric oxygen and amino nitrogen atoms of said morpholine.

8. An adduct of aluminum borohydride with methoxyamine, said adduct possessing a coordinate bond between the aluminum moiety of said aluminum borohydride and the nitrogen atom of said methoxyamine.

9. An adduct of aluminum borohydride with 2,2'-bis-(3-aminopropoxyethyl) ether, said adduct possessing at least one coordinate bond between the aluminum moiety of said aluminum borohydride and an atom of the group consisting of etheric oxygen and amino nitrogen atoms of said ether.

10. A process which comprises reacting a metal borohydride of the group consisting of aluminum borohydride, beryllium borohydride, and zirconium borohydride, with a ligand composed solely of carbon, hydrogen, etheric oxygen, and amino nitrogen atoms in which at least one of said atoms of the group consisting of etheric oxygen and amino nitrogen atoms functions as a Lewis base, under an inert, anhydrous atmosphere, and recovering a metal borohydride adduct of said ligand, as the resulting product, from the reaction medium, said adduct possessing at least one coordinate bond between the metal moiety of said metal borohydride and an atom of the group consisting of etheric oxygen and amino nitrogen atoms of said ligand.

11. The process of claim **10** wherein the reaction is effected at a temperature in the range of from about −64° C. to about +43° C.

12. The process of claim **11** wherein said metal borohydride is aluminum borohydride.

13. The process of claim **12** wherein the maximum concentration of said aluminum borohydride is in slight excess of the quantity that is necessary to react with said ligand, and wherein the resulting product is a liquid adduct of aluminum borohydride and ligand.

14. The process of claim **13** wherein said aluminum borohydride is added, in increments, to said ligand.

15. The process of claim **12** wherein the maximum concentration of said ligand is in slight excess of the quantity that is necessary to react with said aluminum borohydride, and wherein the resulting product is a solid adduct of aluminum borohydride and said ligand.

16. The process of claim **15** wherein said aluminum borohydride is added, in increments, to said ligand.

17. The process of claim **12** wherein essentially stoichiometric amounts of aluminum borohydride and ligand are employed.

References Cited

UNITED STATES PATENTS

2,993,895	7/1961	Withrop	260—247
2,993,894	7/1961	Marcus et al.	260—247
2,993,335	7/1961	Burton et al.	60—35.4
3,020,708	2/1962	Mahan	60—35.4

NICHOLAS S. RIZZO, *Primary Examiner.*

JOSE TOVAR, *Assistant Examiner.*