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RESEARCH MEMORANDUM

THERMAL DECOMPOSITION OF SOME GROUP I, II, AND III METAL ALKYLS

By Louis Rosenblum

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NATIONAL ADVISORY COMMITTEE
FOR AERONAUTICS

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SUMMARY

A mechanism is presented for the thermal decomposition of sodium, lithium, beryllium, magnesium, aluminum, and boron alkyls and for the reverse reaction, the addition of olefins to metal hydrides. These reactions are shown to be nonradical and to probably proceed through a cyclic intermediate. Calculations have been made of the free energies, heats, entropies, and activation energies of reaction for the decomposition of some boron and aluminum alkyls. Decomposition both by the nonradical path and a radical path were considered for purposes of comparison. The nonradical decomposition at 298° to 400° K (25° to 127° C) is not spontaneous, while a radical decomposition is. Estimates of the activation energy indicate that they have lower values for the nonradical decomposition of boron and aluminum alkyls than for a radical decomposition. The implications of aerodynamic heating in relation to the use of metal alkyls as aircraft fuels or ignition sources are discussed. The temperature ranges and decomposition products for the different decomposition paths and methods of controlling decomposition are presented. Also, a new way of preparing alkylated boron hydrides is proposed.

INTRODUCTION

The object of this report is to suggest a possible mechanism for the thermal decomposition of some group I, II, and III metal alkyls and to examine the thermodynamics and kinetics of this reaction. A better understanding of the nature and reactions of metal alkyls is needed in view of their uses in supersonic aircraft and rockets. These uses fall into two main catogories: fuels (refs. 1 to 3) and ignition sources (refs. 3 to 5 and unpublished NACA data). As fuels, metal alkyl compounds are used to give increased heat release and flame speeds over that of hydrocarbon fuels. As high-energy ignition sources, they can be used for engine starting or restarting in case of flameout, or as a fuel additive to promote continuous combustion without external ignition.

Sodium (ref. 6), lithium (ref. 7), beryllium (refs. 8 to 10), magnesium (refs. 11 to 13), and boron (ref. 14) alkyls thermally decompose

under vacuum at 100° to 200° C. The main products are a metal hydride or alkyl metal hydride and an olefin of the same number of carbon atoms as the original alkyl group. The reaction for these thermal decompositions can be written in the general form:

$$MR_a \rightleftharpoons MH_bR_{a-b} + bR_{-H}$$

where

R alkyl group, C_2 or higher

a valence number of metal M

R_{-H} olefin (alkyl group R less one hydrogen atom)

The similarity both in the nature of the products and the experimental conditions suggests that the same mechanism is involved in all these decompositions.

It should be noted that the products may undergo further reaction. For example, in the decomposition of trialkylboranes, if dialkyl boron hydride is initially formed, it will dimerize as follows:

$$2R_2BH \rightarrow R_2B\begin{matrix}H\\ \diagup\ \diagdown\\ H\end{matrix}BR_2$$

This tetraalkyldiborane can then disproportionate to yield an equilibrium mixture of mono-, di-, tri-, and tetralkyldiborane; diborane; and trialkylborane. Also, the olefin product may isomerize; for example, butene-1 formed in the decomposition of tri-n-butylborane (ref. 14) can rearrange to butene-2 under more rigorous decomposition conditions.

DISCUSSION

Mechanism

The metal hydride product of the decomposition can arise only by the transfer of hydrogen from carbon to metal. This hydrogen can be removed in one of two ways: either homolytically as a hydrogen atom or heterolytically as a proton or hydride ion.

If the homolytic reaction is taken first, the following possible reaction paths can be written, using a group II metal alkyl as an example:

$$R_2M \rightarrow RM\cdot + R\cdot \qquad (1)$$

$$RM\cdot \rightarrow M + R\cdot \quad (2)$$

$$R\cdot \rightarrow R_{-H} + H\cdot \quad (3a)$$

$$2R\cdot \rightarrow R_{-H} + RH \quad (3b)$$

$$2R\cdot \rightarrow R\text{-}R \quad (3c)$$

$$R_2M + H\cdot \rightarrow RMH + R\cdot \quad (4)$$

$$R_2M + RM\cdot \rightarrow RMH + RMR\cdot_{-H} \quad (5)$$

$$RMR\cdot_{-H} \rightarrow RM\cdot + R_{-H} \quad (6)$$

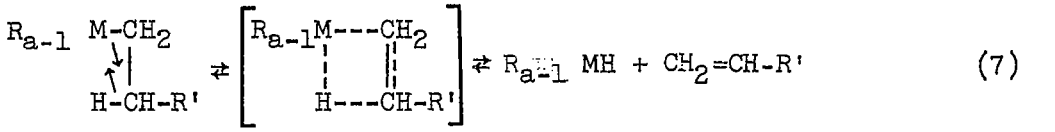
While zinc (ref. 15), mercury (ref. 15), lead (ref. 15), germanium (ref. 15), and cadmium (ref. 16) alkyls are known to decompose as in reactions (1) and (2), the products obtained result from the disproportionation, reaction (3b), and the dimerization, reaction (3c), of the alkyl radical. These products do not correspond to those obtained from the thermal decomposition of sodium, beryllium, magnesium, or boron alkyls. The reaction sequences that will yield the metal hydride and olefin products are either (1), (3a), and (4); (1), (2), (3a), and (4); or (1), (5), and (6).

Since alkyl radicals do not decompose to give a hydrogen atom and an olefin (refs. 17 and 18, reaction (3a)), except at temperatures above 500° C (ref. 19), reaction sequence (1), (3a), and (4) can be disregarded. Similarly, reactions (5) and (6), which depend on RM·, can be shown to be unimportant. For the metal alkyls discussed herein, the first bond dissociation energy D_1 (reaction (1)) should be greater than the second bond dissociation energy D_2 (reaction (2)) (refs. 20 to 22). This being the case, the concentration of RM· will be quite low; and, hence, reaction sequences (1), (5), and (6) will be untenable.

The remaining possibility is the heterolytic removal of hydrogen. This process by itself is energetically improbable unless this initial endothermic step is thermodynamically coupled with an exothermic step (ref. 23). Thus, if a bond-breaking process is coupled with a bond-making process, the energy involved in the total process is small. Furthermore, the activation energy for such a process is less than that required for homolytic dissociation (ref. 24).

A mechanism incorporating this simultaneous bond-making -breaking process can be written by using an activated complex similar to that proposed by Swain and Boules (ref. 25) for the reduction of ketones by

Grignard reagents, by Gee (ref. 26) for hydrogen transfer during the pyrolysis of certain hydrocarbons, and by Wiberg and Bauer (ref. 13) for the pyrolysis of magnesium alkyls:



$$R_{a-1}\ \begin{matrix} M\text{-}CH_2 \\ \downarrow\ \ | \\ H\text{-}CH\text{-}R' \end{matrix} \rightleftharpoons \left[\begin{matrix} R_{a-1}M\text{---}CH_2 \\ \vdots\ \ \| \\ H\text{---}CH\text{-}R' \end{matrix} \right] \rightleftharpoons R_{a-1}MH + CH_2{=}CH\text{-}R' \qquad (7)$$

where

$$R = CH_2\text{-}CH_2\text{-}R'$$

$$R' = \text{alkyl group or H}$$

This decomposition mechanism (reaction (7)) supposes an intramolecular transfer of hydrogen with its electrons from the β-C to the metal, with a transfer of the electron pair from the α-C-M bond to the α-C-β-C bond at the same time. It would be expected that this hydrogen be removed as a hydride ion. The electron deficient character of the metal would provide a driving force for hydride ion removal, while it would not for proton removal.

Metal alkyl hydrides such as alkylated diboranes, pentaboranes, and decaboranes would not decompose by way of reaction (7). In these compounds all the bonding orbitals about the boron are in use. Therefore, there would be no situation comparable to the alkyl boranes where one bonding orbital is available to receive a hydride ion.

Conceivably, a bimolecular hydrogen transfer can be written in place of reaction (7). However, the expectation is that the unimolecular reaction should be favored over the bimolecular reaction. In systems capable of forming three- to six-membered cyclic intermediates, the high effective concentration of one reactive group, H, in the vicinity of a second reactive group, M, greatly increases the probability of the unimolecular reaction (ref. 27).

From this argument, it would be predicted that the more hydrogen on the α-C replaced by methyl groups, the more readily the decomposition reaction should go. The enhanced reactivity would result from a larger concentration of H in the reaction-favored γ-position. Under the same circumstances, a bimolecular mechanism would predict a diminishing reactivity. The increasing bulk of the hydrocarbon residue would sterically hinder the close approach of two molecules.

In the series Me_2Be, $(MeCH_2)_2Be$, $(Me_2CH)_2Be$, and $(Me_3C)_2Be$, it was found that the thermal stability decreases and the ease of reaction, to

give RBeH and BeH_2, increases from left to right (ref. 10). This evidence would appear to favor the unimolecular mechanism. The increase of reaction in this series, however, might well be aided by a weakening of the Be-C bond with increased methylation of the α-C. For example, in the case of the analogous hydrocarbons, C_α-C_β, as the number of methyl groups attached to one of the carbon atoms increases from 0 to 1 to 2 to 3, the bond energy decreases from 84.4 to 82.2 to 77.5 to 74.8, respectively (ref. 28).

The reverse reaction, the addition of a metal alkyl hydride or metal hydride to an olefin, has been investigated for the metal, boron. Hurd (ref. 29) found that diborane reacts with olefins to give trialkylboranes. He proposed, for the addition reaction, essentially the same type of mechanism as is outlined in reaction (7). One carbon of the C-C double bond complexes with a borane molecule, followed by a transfer of a hydride ion from boron to the second carbon of the C-C double bond. He assumes this process repeats itself until all the hydrogens on the borane are exhausted. Alternately, Hurd suggests, the monoalkylborane (RBH_2) initially formed can disproportionate to ultimately yield the trialkylborane.

A kinetic study by Whatley and Pease (ref. 30) of the addition of ethylene to diborane showed that the rate of decrease in the pressure of the system is a function of the 3/2 power of the B_2H_6 concentration. They proposed a mechanism to account for this data involving B_3 type complexes, and equated the rate of decrease of pressure to the rate of increase of BEt_3 concentration:

$$B_2H_6 \rightleftarrows 2BH_3 \tag{8}$$

$$B_2H_6 + BH_3 \rightarrow B_3H_9 \tag{9}$$

$$B_3H_9 + C_2H_4 \rightarrow B_2H_5Et + BH_3 \tag{10}$$

$$B_2H_5Et + BH_3 \rightarrow B_3H_8Et \tag{11}$$

$$B_3H_8Et + C_2H_4 \rightarrow B_2H_4Et_2 + BH_3 \tag{12}$$

$$B_2H_4Et_2 + BH_3 \rightarrow B_3H_7Et_2 \tag{13}$$

$$B_3H_7Et_2 + B_2H_6 \rightarrow 2B_2H_5Et + BH_3 \tag{14}$$

$$B_3H_7Et_2 + C_2H_4 \rightarrow B_2H_3Et_3 + BH_3 \tag{15}$$

and so forth.

It is also possible to arrive at a dependence of the rate of decrease of pressure on the 3/2 power of the diborane concentration from the mechanism proposed by Hurd with the added assumptions of competative reactions between diborane and ethylene for the intermediate products and a steady-state condition for all the reaction intermediates. The rate of decrease of pressure is equated with the rate of decrease of concentration of diborane:

$$B_2H_6 \rightleftarrows 2BH_3 \tag{8}$$

$$BH_3 + C_2H_4 \rightarrow BH_2Et \tag{16}$$

$$BH_2Et + C_2H_4 \rightarrow BHEt_2 \tag{17}$$

$$BH_2Et + B_2H_6 \rightarrow B_2H_5Et + BH_3 \tag{18}$$

$$B_2H_5Et \rightarrow BH_3 + BH_2Et \tag{19}$$

$$BHEt_2 + C_2H_4 \rightarrow BEt_3 \tag{20}$$

$$BHEt_2 + B_2H_6 \rightarrow B_2H_4Et_2 + BH_3 \tag{21}$$

and so forth.

The possibility of the presence of B_1, B_2, and even B_3 compounds coupled with their involved disproportionation, dissociation, and equilibria reactions make the determination of a mechanism extremely difficult.

Thermodynamics and Kinetics

It would be helpful to calculate the free energies of the thermal decomposition reactions so that conditions can be determined for which these reactions are thermodynamically feasible. There are only two metals, at present, for which enough data are available or can be reasonably estimated to make these calculations. These are boron and aluminum. Table I (see appendix for methods of calculation) contains the free energies of the reaction

$$MR_{3(g)} \rightleftarrows MHR_{2(g)} + R_{-H(g)} \tag{7a}$$

for four boron and two aluminum alkyls at 298°, 400°, and 400° K at 0.01 atmosphere.

It is immediately apparent from the positive values of the free energies ΔF° that the reaction will not go spontaneously in the direction indicated. However,

$$\Delta F_{298} = \Delta F^{\circ}_{298} + RT \ln \frac{C_B^2}{C_A}$$

where

C_B concentration of R_{-H} = concentration of MHR_2 (reaction (7a))

C_A concentration of MR_3

By sufficiently lowering the concentration of the products MHR_2 and R_{-H}, the free energy of the reaction can be made negative and the reaction can proceed in the direction indicated. The concentration of the products can be lowered by two general methods: (1) physically, by removing or immobilizing the products, for example, by continuously pumping under vacuum, freezing out, or adsorbing the volatile products; and (2) chemically, by further reacting the products, for example, hydrogenation of the olefin, as it is formed, to saturated hydrocarbon.

The conclusions reached in the preceding discussion are, of course, independent of the particular mechanism of the reaction and depend only on the initial and final states.

The free energy of an alternate decomposition reaction

$$MR_{3(g)} \rightarrow M_{(s)} + xRH + yR_{-H} + \frac{z}{2} RR \qquad (22)$$

where

$$x + y + z = 3$$

which presumably goes by way of a free radical mechanism, should also be considered. Although this type of reaction probably does not take place to any appreciable extent with boron and aluminum alkyls below 700° and 400° C, respectively, it no doubt becomes important at higher temperatures. The free energies for this reaction for two boron and two aluminum alkyls are listed in table II (see appendix and table III). As indicated by the free energies, these reactions are all spontaneous at 400° K.

Since the activation energies in the case of boron and aluminum alkyls are assumed to be higher for the radical reaction (22) than for

the nonradical reaction (7a), decomposition by the radical path would not be expected. This last assumption can be given some additional degree of validity by making a rough estimate of the energy requirements for each reaction.

For the radical decomposition of MR_3 (reaction (22)), the activation energy will be approximately equal to the energy needed to break the first M-R bond:

$$MR_3 \rightleftarrows MR_2^{\bullet} + R^{\bullet} \qquad (23)$$

assuming that the reverse-reaction activation energy is approximately zero (ref. 31, p. 104). By using the average bond energies $\overline{D}$ (table IV) as minimum values for the MR_2-R bond energies, the activation energies would be >85 kcal/mole and >57 kcal/mole, respectively, for boron triethyl and aluminum triethyl. Furthermore, the method of Long and Norrish (ref. 20), from a consideration of the excited states of the atoms involved, gives values of 112 kilocalories per mole and 83 kilocalories per mole for boron triethyl and aluminum triethyl, respectively, for the energy of removal of the first ethyl radical.

For the nonradical cyclic decomposition (reaction (7)), the difference between the activation energy of the forward reaction E_1 and the reverse reaction E_2 is equal to the heat of the reaction ΔH (see table III and appendix). The reverse reaction E_2 may be estimated by Hirschfelder's rule (ref. 32) as 28 percent of the energy of the bonds broken (table IV).

For BEt_3,

$$E_1 = \Delta H + E_2 = 30 + 37 = 67 \text{ kcal/mole}$$

For $AlEt_3$,

$$E_1 = \Delta H + E_2 = 18 + 33 = 51 \text{ kcal/mole}$$

It should be stressed that these values are only approximate. Even so, it appears from the preceding calculations that the nonradical mode of decomposition is energetically more favorable than the radical.

Practical Implications

One of the major problems encountered in high-speed flight is aerodynamic heating. The heat generated by the adiabatic compression of the air not only affects the airframe and components, but the fuel as well.

The fuel may be heated directly by heat transfer to the fuel tank, or in certain applications the fuel may be further heated when used as a coolant fluid in heat exchangers. But, regardless of the manner in which the fuel is heated, the same problem presents itself, namely, the thermal decomposition of the fuel. It then is important to know at what temperature the fuel will decompose, the products of decomposition, and the rates of their formation.

If metal alkyls are used in an aircraft as fuel, fuel additive, or an ignition source, heat will bring about decomposition by either a radical or nonradical path, depending on the compound, temperature, and pressure. With materials such as boron triethyl and aluminum triethyl, at temperatures up to approximately 700° and 400° C, respectively, nonradical decomposition should predominate. The products of this decomposition would be the metal ethyl hydride and ethylene. However, it should be possible to completely suppress this reaction, as can be seen from the reaction equilibrium, by preventing the ethylene formed from venting out of the fuel tank. Instead, the tank should be unvented or pressurized with ethylene.

In high-temperature applications the advantages gained by the aircraft through the use of a metal alkyl would have to be weighed against the adverse effect of the additional weight required for a pressure tank, tank insulation, or a tank cooling system. Where the metal alkyl can be used in relatively small quantities, as an ignition source or for a temporary power boost, pressure tanks might be feasible. In a situation such as this, a tank designed to take pressures up to 150 pounds per square inch, for example, could be used up to 200° C for triethyl borane and up to 325° C for triethyl aluminum.

If material losses can be tolerated, then the fuel tank can be vented. Thermal decomposition products formed in the fuel tank should not cause any special difficulties in subsequent use, and the heat release and hypergolic properties of the metal alkyl should remain essentially the same.

However, as previously mentioned, high-temperature conditions are not encountered only in the fuel tank. Fuel passing through heat exchangers or spray nozzles may be subjected to temperatures in excess of 400° C. Above about 700° C with triethyl boron and about 400° C with triethyl aluminum, the radical mechanism should come into play, resulting in the production of free metal, ethane, ethylene, and polymeric materials. Some of these products may clog fuel lines, filters, and spray nozzles.

Metal alkyls, for which the M-C bond dissociation energy is low, will decompose by a radical mechanism at fairly low temperatures. Thallium and zinc alkyls, for example, decompose at about 90° C.

Although the compounds are spontaneously inflammable and can be used as ignition initiators (ref. 33), they would not be acceptable for aircraft use from thermal stability considerations.

Most of the aspects of the thermal decomposition of metal alkyls, just presented, show it to be an undesirable reaction. However, there is one part of the thermal decomposition picture which may prove quite helpful in developing supersonic-aircraft fuels. This is the nonradical decomposition of the boron alkyls:

$$BR_3 \rightleftharpoons BHR_2 + R_{-H}$$

This can be seen to offer a novel way of synthesizing boron hydrides. (At present, boron hydrides are prepared mainly by use of costly metal hydrides.) The boron alkyl hydrides produced in the preceding reaction can be pyrolysed to yield alkylated pentaboranes and decaboranes.

CONCLUSIONS

In general, it would be expected that nonradical decomposition will predominate in molecules where the M-C bond dissociation energy is large. The activation energy E of the rate equation

$$k = Ae^{-E/RT}$$

(where R is the universal gas constant and T is absolute temperature) would be smaller for the nonradical process than for the radical process. However, the frequency factor A would be smaller for the cyclic nonradical mechanism than for the radical mechanism. This is the result of a decrease in entropy when going from a linear to a cyclic form. But, it is expected that the over-all result would be that the nonradical process be favored as to the specific rate constant k.

In going down a periodic group from the light to heavy members, it is found that the M-C bond dissociation energy markedly decreases (ref. 34). Then, for the heavier members of a group, the value of E for both reactions should not be too different, while the value of A will be lower for the cyclic mechanism. The specific rate constant for the radical reaction should then be greater than for the nonradical reaction.

There is, no doubt, an intermediate region in which the activation energies and frequency factors for both processes combine to give specific rate constants that are not too different. In this region of a periodic group, both reactions, the radical and the nonradical, should occur; and products from both reactions will be obtained. Actually, parallel reactions may take place from one end of a group to another to

a greater or lesser extent. Experimental information concerning the activation energies and the frequency factors would be needed to predict this quantitatively.

For the case of metal alkyls when the alkyl group is methyl, the cyclic mechanism would require the formation of a three-membered ring intermediate. This would result in a slightly higher value for A and a much higher value for E, the consequence being that the radical reaction would preferentially occur (ref. 35).

Lewis Flight Propulsion Laboratory
National Advisory Committee for Aeronautics
Cleveland, Ohio, December 19, 1956

APPENDIX - THERMOCHEMICAL CALCULATIONS

Heat of Formation

The heats of formation of compounds listed in table III,

$$\Delta H_f^\circ = \sum \Delta H_{f,prod.}^\circ - \sum \overline{D}$$

where

ΔH_f° heat of formation of compound BH_xR_y

$\Delta H_{f,prod.}^\circ$ heat of formation of products B, H, and R

$\overline{D}$ average energy of bond B-H or B-R

were calculated from the dissociation reaction of the compound:

$$BH_xR_{y(g)} \rightarrow B_{(g)} + xH_{(g)} + yR_{(g)}$$

Entropy of Formation

The entropies of formation

$$\Delta S_f^\circ = S_{comp.}^\circ - \sum S_{elements}^\circ$$

where

ΔS_f° entropy of formation of compound BH_xC_y

$S_{comp.}^\circ$ entropy of compound BH_xC_y

$S_{elements}^\circ$ entropy of elements in their standard states

were calculated on the basis of the following reaction:

$$B_{(c)} + \frac{x}{2} H_{2(g)} + yC_{(graphite)} \rightarrow BH_xC_{y(g)}$$

The values of $S_{comp.}^\circ$ are listed in tables V and VI.

The following values of $S^{\circ}_{elements}$ were used:

$B_{(c)}$ (ref. 36)	1.403
$C_{(graphite)}$ (ref. 37)	1.3609
$H_{2(g)}$ (ref. 37)	31.211
$Al_{(s)}$ (ref. 38)	6.8

Free Energy of Formation

The free energies of formation were calculated from the equation

$$\Delta F^{\circ}_{f} = \Delta H^{\circ}_{f} - T\,\Delta S^{\circ}_{f}$$

where

ΔF°_{f} free energy of formation at temperature T

T temperature, $^{\circ}K$

Free Energy of Reaction

The free energy of reaction was calculated as follows:

$$\Delta F^{\circ}_{r} = \sum \Delta F^{\circ}_{f,prod.} - \sum \Delta F^{\circ}_{f,react.}$$

where

ΔF°_{r} free energy of reaction at 298° K

$\Delta F^{\circ}_{f,prod.}$ free energy of formation of products at 298° K

$\Delta F^{\circ}_{f,react.}$ free energy of formation of reactants at 298° K

The free energy of reaction at 400° K was calculated from the equation

$$\Delta F^{\circ}_{r} = \Delta H^{\circ}_{r} - T\,\Delta S^{\circ}_{r}$$

where

ΔH°_{r} heat of reaction

ΔS°_{r} entropy of reaction

assuming no appreciable change in the ΔH_r^o or ΔS_r^o values from 298° to 400° K.

The free energy at 400° K and 0.01 atmosphere was calculated as follows:

$$\Delta F_{400,0.01\ atm.} = \Delta F^o_{400} + RT \ln \frac{0.01^2}{1}$$

Average Bond Energies

The average bond energy $\overline{D}$ was calculated as follows:

$$\overline{D}(B - R) = \frac{\Delta H_r}{3}$$

where

ΔH_r heat of dissociation reaction:

$$BR_{3(g)} \rightarrow B_{(g)} + 3R_{(g)}$$

The value for $\overline{D}$(Al-H) was calculated from the Pauling geometric mean equation (ref. 39) as follows:

$$\overline{D}(Al\text{-}H) = \sqrt{D(Al\text{-}Al)\ D(H\text{-}H)} + 23.06(X_{Al} - X_H)^2$$

$$= \sqrt{43.8 \times 104.2} + 23.06(1.5 - 2.1)^2$$

$$= 75.8 \text{ kcal/mole}$$

All values for D and X were obtained from reference 40.

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TABLE I. - CALCULATED VALUES OF FREE ENERGY OF NONRADICAL

REACTION $MR_{3(g)} \rightarrow MHR_{2(g)} + R_{-H(g)}$

Alkyl group, R	ΔF°_{298}, kcal/mole	ΔF°_{400}, kcal/mole	$\Delta F_{400,0.01\ atm}$, kcal/mole
M = Boron			
Methyl[a]	17	16	9
Ethyl	21	18	11
n-Propyl	19	15	8
n-Butyl	21	17	10
M = Aluminum			
Methyl[a]	9	7	0
Ethyl	12	9	2

[a]For methyl compounds the reaction is $MMe_{3(g)} \rightarrow MHMe_{2(g)} + 1/2\ C_2H_{4(g)}$.

TABLE II. - CALCULATED VALUES OF FREE ENERGY OF RADICAL REACTION

Metal, M	ΔF°_{298}, kcal/mole	ΔF°_{400}, kcal/mole
$MMe_{3(g)} \rightarrow M_{(s)} + 1\frac{1}{2}\ C_2H_{6(g)}$		
B	-3	-4
Al	-20	-19
$MEt_{3(g)} \rightarrow M_{(s)} + xC_2H_{6(g)} + yC_2H_{4(g)} + zC_4H_{10(g)}$[a]		
B	-3	-6
Al	-21	-23

[a]For purposes of calculation, the following values were used: $x = y = 1/2$; $z = 1$. These values are reasonable in view of the experimental data on the decomposition of mercury alkyls (ref. 41). From $z = 0$ to $z = 1\frac{1}{2}$ for BEt_3 and $AlEt_3$, respectively, the ΔF°_{298} values are +9 to -9 kcal/mole and 0 to -28 kcal/mole.

TABLE III. - THERMODYNAMIC PROPERTIES OF GASEOUS B, Al, C AND H COMPOUNDS AT 25° C

Compound	Heat of formation, ΔH_f°, kcal/mole	Entropy of formation, ΔS_f°, cal/(deg)(mole) (a)	Free energy of formation, ΔF_f°, kcal/mole	Entropy, S°, cal/(deg)(mole)
$B(CH_3)_3$	[b] -29.8	-69.4	[b] -9.1	[b] 76.6
$B(C_2H_5)_3$	[c] -38.0	-140	[c] 3.7	[d] 104.9
$B(n\text{-}C_3H_7)_3$	[c] -53.7	-209	[a] 9	[e,f] 132
$B(n\text{-}C_4H_9)_3$	[c] -70.8	-278	[a] 12	[e] 161
$BH(CH_3)_2$	[a] -14	-48	[a] 0	[e] 64
$BH(C_2H_5)_2$	[a] -20	-96	[a] 8	[e] 84
$BH(n\text{-}C_3H_7)_2$	[a] -30	-141	[a] 12	[e] 103
$BH(n\text{-}C_4H_9)_2$	[a] -40	-186	[a] 15	[e] 123
$Al(CH_3)_3$	[g] -13.3	-71	[a] 8	[e] 81
$Al(C_2H_5)_3$	[a] -21	-141	[a] 21	[e] 109
$AlH(CH_3)_2$	[a] -8	-51	[a] 9	[e] 68
$AlH(C_2H_5)_2$	[a] -13	-97	[a] 16	[e] 87
CH_3	[h] 32			
C_2H_5	[h] 25			
$n\text{-}C_3H_7$	[h] 22			
$n\text{-}C_4H_9$	[h] 19			
C	[i] 171.7			
H	[i] 52.1			
B	[j] 140.9			
Al	[i] 75.0			

[a] See appendix for method of calculation.

[b] Ref. 42.

[c] Ref. 36.

[d] Ref. 43.

[e] See table VI, footnote b.

[f] Value of 131 cal/(deg)(mole) was calculated by N.B.S. (ref. 36) by method of comparison with corresponding paraffin hydrocarbon.

[g] Ref. 20.

[h] Values calculated from dissociation energies given in ref. 44.

[i] Ref. 38.

[j] Ref. 45.

TABLE IV. - AVERAGE BOND ENERGIES $\overline{D}$

Bond	$\overline{D}$, kcal/mole
B-CH_3	[a]89
B-C_2H_5	[a]85
B-n-C_3H_7	[a]87
B-n-C_4H_9	[a]89
B-H	[a,b]93
Al-CH_3	[c]61.4
Al-C_2H_5	[d]57
Al-H	[a]76
C-C	[e]84.5
C=C	[e]125

[a]See appendix for method of calculation.
[b]Ref. 45.
[c]Ref. 20.
[d]Estimated from trend shown in boron, mercury, cadmium and zinc alkyls from $\overline{D}$(M-CH_3) to $\overline{D}$(M-C_2H_5).
[e]Ref. 46.

TABLE V. - ENTROPY OF GASEOUS HYDRIDES OF PERIOD I AND II ELEMENTS AT 25° C

Period I compound	Entropy, S^o_I, cal/(deg)(mole) (a)	Period II compound	Entropy S^o_{II}, cal/(deg)(mole) (a)	$S^o_{II} - S^o_I$, cal/(deg)(mole)
HF	41.47	HCl	44.62	3.1
H_2O	45.11	H_2S	49.15	4.04
H_3N	46.01	H_3P	50.2	4.2
H_4C	44.50	H_4Si	48.7	4.2
H_3B	[b]45	H_3Al	[c]49	---
HLi	40.77	HNa	44.93	4.16

[a]Values from ref. 38.
[b]Ref. 36.
[c]Calculated by addition of $S^o_{II} - S^o_I$ (4 cal/(deg)(mole)) to entropy of BH_3.

TABLE VI. - GASEOUS ENTROPIES OF ALKYLATED COMPOUNDS OF PERIOD I AND II ELEMENTS AT 25° C

Period I compound	Entropy, S°_{I}, cal/(deg)(mole)			Period II compound	Entropy, S°_{I}, cal/(deg)(mole)		
	Experimental[a]	Calculated[b]	Difference		Experimental[a]	Calculated[b]	Difference
CH_3F	53.3	52.9	-0.4	CH_3Cl	55.97	56.0	0
CH_3OH	56.8	56.5	-.3	CH_3SH	60.91	60.6	-.3
CH_3NH_2	57.73	57.4	-.3	CH_3PH_2	------	61.6	---
CH_3CH_3	54.85	55.9	1.0	CH_3SiH_3	------	60.1	---
CH_3BH_2	------	56.4	----	CH_3AlH_2	------	60.4	---
$(CH_3)_2O$	63.72	64.5	.8	$(CH_3)_2S$	68.28	68.6	.3
$(CH_3)_2NH$	65.30	65.4	.1	$(CH_3)_2PH$	------	69.6	---
$(CH_3)_2CH$	64.51	63.4	-.6	$(CH_3)_2SiH$	------	68.1	---
$(CH_3)_2BH$	------	64.4	----	$(CH_3)_2AlH$	------	68.4	---
$(CH_3)_3N$	------	-----	----	$(CH_3)_3P$	------	-----	---
$(CH_3)_3CH$	70.42	[c]73.6	3.2	$(CH_3)_3SiH$	------	[d]74.6	---
$(CH_3)_3B$	[e]76.60	[c]74.1	-2.5	$(CH_3)_3Al$	------	[d]80.8	---
$(C_2H_5)O$	------	83.9	----	$(C_2H_5)_2S$	[f]87.96	88.0	0
$(C_2H_5)_2NH$	------	84.8	----	$(C_2H_5)_2PH$	------	89.0	---
$(C_2H_5)_2CH$	83.27	83.3	0	$(C_2H_5)_2SiH_2$	------	87.5	---
$(C_2H_5)_2BH$	------	83.8	----	$(C_2H_5)_2AlH$	------	87.8	---
$(C_2H_5)_3N$	------	-----	----	$(C_2H_5)_3P$	------	-----	---
$(C_2H_5)_3CH$	98.47	[c]102.7	4.2	$(C_2H_5)_3SiH$	------	[d]102.6	---
$(C_2H_5)_3B$	[g]104.9	[c]103.0	-1.9	$(C_2H_5)_3Al$	------	[d]109.1	---

[a]Values from refs. 37 and 38, except where noted.

[b]Values calculated from following empirical equations: For one methyl group, $S^{\circ} = S^{\circ}_{hydride} + 11.4$; for more than one methyl or ethyl group, where n = number of carbon atoms, $S^{\circ} = S^{\circ}_{hydride} + 9.7n$.

[c]The agreement between the calculated and experimental values is rather poor, as expected, since the empirical equations (footnote b) were derived for molecules analogous to normal hydrocarbons. n-Paraffin hydrocarbons exhibit a linear relation between the entropy and the number of carbon atoms (ref. 47). Branched-chained hydrocarbons do not fit this series. Therefore, in compounds where there is tri- and tetra-substitution on the central atom, the fit with the empirical equation will be poor.

[d]Values calculated by addition of entropy increment between periods II and I, 4.2, to entropy of related period I compound (table V).

[e]Value from ref. 42.

[f]Ref. 48.

[g]Value from ref. 43.

[redacted]