Journal of Organometallic Chemistry, 76 (1974) 171—201
© Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

THE HEATS OF FORMATION OF ALUMINUM ALKYLS AND RELATED COMPOUNDS

MARTIN B. SMITH
Chemical Research and Development, Ethyl Corporation, Baton Rouge, Louisiana (U.S.A.)

(Received September 14th, 1973; in revised form February 25th, 1974)

Summary

In order to resolve conflicts in published heats of formation of aluminum alkyls and related compounds, a one-constant equation (the "Displacement Rule") has been derived relating ΔH_f^0(M, g) (M = monomer) of primary alkyls (R $\neq$ Me) of any element to ΔH_f^0(g) of RH. The rule, which permits the calculation of ΔH_f^0(M, g) of all the primary alkyls (R $\neq$ Me) of an element, including mixed alkyls and "iso"-alkyls, yields values that are practically identical with those developed from the Allen bond-energy scheme. It has been shown that for many metals the rule can be extended to include the methyl compounds. Values of ΔH_f^0(M, g) and ΔH_f^0(l) have been tabulated for a number of primary alkyls of Zn, Hg, B, Al and Sn. For straight-chain R groups of two or more C atoms, the results are well represented by equations of the form $-\Delta H_f^0(25°) = A + B(N - 2)$ kcal/gfw (N = no. of C atoms). For the gaseous monomers, the constants A and B are as follows: R_2Zn: -8.3, 9.8_6; R_2Hg: -17.8, 9.8_6; R_2AlH: 11.1, 9.8_6; R_3B: 36.4, 14.7_9; R_3Al: 27.9, 14.7_9; R_4Sn: 13.9, 19.7_2. Experimental values of ΔH_f^0(l) have been determined for eight ethylaluminum halides by the measurement of heats of redistribution. These results have been used to prepare tables of ΔH_f^0(l) values for the primary alkylaluminum halides. For these liquid dimers, the constants A and B are as follows: R_2AlCl: 92.1, 12.0; R_2AlBr: 78.6, 12.0; R_2AlI: 61.1, 12.0; $RAlCl_2$: 128.9, 6.0; $RAlBr_2$: 101.8, 6.0; $RAlI_2$: 67.6, 6.0; $R_3Al_2Cl_3$: 221.6, 18.0; $R_3Al_2Br_3$: 181.0, 18.0; $R_3Al_2I_3$: 129.2, 18.0. After comparison of the ΔH_f^0(l) values for the chlorides with corresponding literature values, it has been demonstrated that most of the literature values (all the values from heat of combustion measurements) are thermodynamically inconsistent, unreliable and in complete disagreement with experience.

Introduction

During the past twenty-odd years, the commercial importance of organoaluminum compounds has been growing rapidly. Among the classes of compounds involved in this growth are the aluminum trialkyls, the alkylaluminum halides (including the dialkylaluminum halides, the monoalkylaluminum dihalides and the sesquihalides) and the dialkylaluminum hydrides. Within each class there is interest, both theoretical and practical, in the longer chain members as well as in the methyl and ethyl compounds. It is important that valid standard heats of formation be established for these compounds.

A valid set of ΔH_f^0 values must satisfy three requirements. First, the ΔH_f^0 values for the compounds belonging to each class must be thermodynamically consistent: within the class, $-\Delta H_f^0(l)$* should increase uniformly with increasing chain length. (The increments in $-\Delta H_f^0(M, g)$* should be practically constant beginning with R = Et. The value of the constant increment for a given class should depend only upon the number of alkyl groups in the class formula.) Second, the ΔH_f^0 values must show thermodynamic consistency from class to class: the different classes are interrelated (via redistribution reactions, for example), hence their ΔH_f^0 values are also interrelated. Third, heats of known reactions calculated from the ΔH_f^0 values must agree at least reasonably well with experience.

Serious discrepancies exist among the experimental $\Delta H_f^0(l)$ values presently available. Values reported for Et_3Al differ by as much as 19 kcal (Table 9). Other differences in observed values are: 23 for i-Bu_3Al (Table 9); 42 for Et_2AlCl (Table 14); 25 for Et_2AlH and 27 kcal for i-Bu_2AlH (Table 11). Observed $\Delta H_f^0(l)$ values for the R_2AlCl series from a single source [1] vary erratically with increasing chain length (Table 14) and hence are not self-consistent thermodynamically. The same is true for the $RAlCl_2$ series (Table 17) and the $R_3Al_2Cl_3$ series (Table 20).

The purpose of this paper is to resolve these discrepancies and to develop sets of ΔH_f^0 values that satisfy all three requirements. A simple relationship (the "Displacement Rule") will first be derived which facilitates not only the comparison of experimental $\Delta H_f^0(M, g)$ values for different primary alkyls ($R \neq Me$) of any given element, but also the calculation of "best values" of $\Delta H_f^0(M, g)$ for all the primary alkyls ($R \neq Me$) of the element. The rule will be used in developing tables of ΔH_f^0 values for the primary alkyls of boron, zinc, mercury and tin. It will be shown that for these four metals (and presumably for various other metals, as well), the rule can be extended to include the methyl compounds. The extended rule will be used to develop tables of ΔH_f^0 values for aluminum alkyls and dialkylaluminum hydrides.

New experimental values of $\Delta H_f^0(l)$ will be presented for the following ethylaluminum halides: Et_2AlCl, Et_2AlBr and Et_2AlI; $EtAlCl_2$, $EtAlBr_2$ and $EtAlI_2$; $Et_3Al_2Cl_3$ and $Et_3Al_2Br_3$. These results will be used to develop tables of ΔH_f^0 values for the corresponding primary alkylaluminum halides.

The "Displacement Rule"

Let X represent any element which forms primary alkyl compounds. We will limit ourselves, for the moment, to compounds each containing only one

---

* ΔH_f^0 and ΔH_v^0, always in kcal/gfw, refer to the values at 25°. Subscripts d and v denote dissociation (to monomer) and vaporization; g and l: gas and liquid; M, D and T: monomer, dimer and trimer.

kind of alkyl group. Each such compound can be represented by the formula $(R'CH_2)_m X$ where R' is an appropriate alkyl group (R) or hydrogen and m is 1—4. Consider the (hypothetical) reaction (eqns. 1 and 2) at 25° between X (in its standard state) and a gaseous alkane to form the corresponding primary alkyl (gaseous monomer) and molecular hydrogen. The "Displacement Rule"*

$$X(\text{std. state}) + m\ R'CH_3(g) \rightarrow (R'CH_2)_m X(M, g) + \frac{m}{2} H_2(g) \tag{1}$$

$$\Delta H = \Delta H_{X(R\ )} = \Delta H_f^0[(R'CH_2)_m X(M, g)] - m\Delta H_f^0[R'CH_3(g)] \tag{2}$$

states that the heat of this "displacement reaction," $\Delta H_{X(R')}$, has the same value $\Delta H_{X(R)}$ (to a good degree of approximation) for R' = any alkyl group R**. [$\Delta H_{X(H)}$, the value of $\Delta H_{X(R')}$ for $R' = H$, may or may not be equal to $\Delta H_{X(R)}$.]

Assuming, for the moment, that the Displacement Rule is valid, values of $\Delta H_{X(R)}$ can be calculated from individual experimental values of $\Delta H_f^0[(RCH_2)_m X(M, g)]$. A "best value" of $\Delta H_{X(R)}$, $\overline{\Delta H}_{X(R)}$, can be determined by a suitable averaging process. "Best values" of $\Delta H_f^0[(RCH_2)_m X(M, g)]$ can now be calculated for all R groups (except as noted previously) using eqn. 3. In applying eqns. 2 and 3, observed values of $\Delta H_f^0[RCH_3(g)]$ are used for the alkanes

$$\Delta H_f^0[(RCH_2)_m X(M, g)] = \overline{\Delta H}_{X(R)} + m\Delta H_f^0[RCH_3(g)] \tag{3}$$

(Table 2) except that "smoothed" values*** are substituted in three cases. For propane, —25.17 kcal is used in place of the observed value of —24.82. The value used for butane is —30.10 kcal (observed value —30.15) and for pentane —35.03 (observed value —35.00). (Analysis of available thermochemical data indicates that the seemingly anomalous observed value for propane is not "carried into" propyl compounds and that improved results are obtained when the smoothed value is substituted for it.)

For the special case in which R is a normal straight-chain alkyl group, the validity of the Displacement Rule follows at once from the "inter-series increment" method of estimating $\Delta H_f^0(g)$. (See, for example, Cox and Pilcher [2], p. 521). The validity of the rule for the general case is also easily demonstrated. For example, the bond-energy scheme described by Allen [3] and Skinner [4] has been shown [4, 5] to correlate very well with available heat of formation data on several series of alkyl compounds. When this sbheme is used to evaluate $\Delta H_{X(R)}$, all the terms which depend on the size and configuration of the alkyl group R cancel out, leaving $\Delta H_{X(R)}$ equal to a constant. To illustrate, let X = boron or aluminum (in which case $m = 3$) and let N = number of

---

[*] It is recognized that the "Displacement Rule" does not embody any new principles. However, it is a useful tool and has been given this name for convenience. In addition, it leads to the proposed "Extended Displacement Rule for Metals" (to be described in this paper) which, if valid, perhaps does advance a new principle.

[**] It is assumed that R and X are such that no new steric effects (i.e. steric effects not already present in RCH_3) are encountered in the formation of $(RCH_2)_m X$. For example, R should probably not be allowed to be i-Pr when X is boron.

[***] Obtained from a plot a $\Delta H_f^0(g)$ vs. carbon number. After substitution of the 3 smoothed values, the increment in $\Delta H_f^0(g)$ between successive alkanes is either 4.92 or 4.93 kcal, beginning with ethane (Table 2).

carbon atoms per alkyl group ($N \geqslant 1$): $\Delta H_f^0[(C_NH_{2N+1})_3X(M, g)] = -3B_{XC} - 3(N-1)B_{CC} - 3(2N+1)B_{CH} - 3b_3\Gamma_{CCC} - b_3'\Gamma_{CCX} - 3\Gamma_{CXC} - 3c_4\Delta_{CCC} - \Delta_{CCC}^{X} + 3[S] + \Delta H_f^0[X(g)] + 3N\Delta H_f^0[C(g)] + 3(2N+1)\Delta H_f^0[H(g)]$

$$\Delta H_f^0[C_NH_{2N+2}(g)] = -(N-1)B_{CC} - (2N+2)B_{CH} - b_3\Gamma_{CCC} - c_4\Delta_{CCC} + [S] + N\Delta H_f^0[C(g)] + (2N+2)\Delta H_f^0[H(g)]$$

$$\Delta H_{X(R')} = \Delta H_f^0[(C_NH_{2N+1})_2X(M,g)] - 3\Delta H_f^0[C_NH_{2N+2}(g)] = -3B_{XC} + 3B_{CH} - b_3'\Gamma_{CCX} - 3\Gamma_{CXC} - \Delta_{CCC}^{X} + \Delta H_f^0[X(g)] - 3\Delta H_f^0[H(g)]$$

Since the bond energies (B_{XC} and B_{CH}), the interaction parameters (Γ_{CCX}, Γ_{CXC} and Δ_{CCC}^{X}) and the heats of formation are all constants, the expression may be abbreviated to:

$$\Delta H_{X(R')} = k_1 - b_3'k_2$$

where k_1 and k_2 are constants and b_3' is the number of C—C—X interactions. For all values of $N \geqslant 2$, the value of b_3' is 3. Since $\Delta H_{X(R)} = k_1 - 3k_2$ = a constant, it follows that the Displacement Rule is valid for $m = 3$*. For $N = 1$, the value of b_3' is zero so that $\Delta H_{X(H)} = k_1 = \Delta H_{X(R)} + 3\Gamma_{CCX}$. It follows that $\Delta H_{X(H)} = \Delta H_{X(R)}$ if, and only if, $\Gamma_{CCX} = 0$. The same results are obtained when m assumes other values except that, in general:

$$\Delta H_{X(H)} = \Delta H_{X(R)} + m\Gamma_{CCX} \tag{4}$$

The important parameter Γ_{CCX} may therefore be evaluated using eqn. 5.

$$\Gamma_{CCX} = \frac{1}{m}[\Delta H_{X(H)} - \Delta H_{X(R)}] \tag{5}$$

If, due to an insufficiency of reliable data, either $\Delta H_{X(H)}$ or $\Delta H_{X(R)}$ is known (but not both), the other can be calculated from eqn. 4 provided a reliable estimate can be obtained for Γ_{CCX}. The electronegative elements have positive values of Γ_{CCX}. For nitrogen, sulfur and the halogens, the Γ_{CCX} values fall in the range +3.0 to 4.3 kcal [2], while Γ_{CCO} is higher at +5.7. As will be shown subsequently, the Γ_{CCX} values for a number of the electropositive elements are approximately zero.

Since many elements are capable of forming discrete mixed primary alkyls, it is useful to state the Displacement Rule in a more generalized form. For a tetravalent element, for example, each compound, whether a "pure" or a mixed alkyl, can be represented by the formula $(R_a'CH_2)(R_b'CH_2)(R_c'CH_2)(R_d'CH_2)X$, where each R_i' is an appropriate alkyl group or hydrogen and duplication is permissible. The displacement reaction is written as eqns. 6 and 7.

$$X(\text{std. state}) + R_a'CH_3(g) + R_b'CH_3(g) + R_c'CH_3(g) + R_d'CH_3(g) \rightarrow (R_a'CH_2)(R_b'CH_2)(R_c'CH_2)(R_d'CH_2)X(M, g) + 2H_2(g) \tag{6}$$

---

* Assuming that the Allen Scheme is applicable to the system in question.

$$\Delta H = \Delta H_{X(R_i')} = \Delta H_f^0[(R_a'CH_2)(R_b'CH_2)(R_c'CH_2)(R_d'CH_2)X(M, g)] \\ - \Delta H_f^0[R_a'CH_3(g)] - \Delta H_f^0[R_b'CH_3(g)] - \Delta H_f^0[R_c'CH_3(g)] - \Delta H_f^0[R_d'CH_3(g)] \tag{7}$$

The "Displacement Rule for Mixed Alkyls" states that $\Delta H_{X(R_i')}$ has the same value (to a good degree of approximation) for any set of four alkyl groups R_a', R_b', R_c' and R_d'. Although no formal proof will be given, the validity of the rule for mixed alkyls is easily demonstrated in the same fashion as was the rule for "pure" alkyls.

It is noted that when $R_a' = R_b' = R_c' = R_d'$ (= R'), eqn. 6 reduces to eqn 1, and eqn. 7 to eqn. 2, with $m = 4$, so that the rule for "pure" alkyls is contained in the rule for mixed alkyls. Since $\Delta H_{X(R_i)} = \Delta H_{X(R)}$, individual experimental values of $\Delta H_{X(R_i)}$, if any, can be combined with the experimental values of $\Delta H_{X(R)}$ in the averaging process to determine $\overline{\Delta H}_{X(R)}$. Best values of ΔH_f^0(g) of mixed alkyls can be calculated from equation 7, or a suitable modification, using $\Delta H_{X(R_i)} = \overline{\Delta H}_{X(R)}$.

Application of the Displacement Rule to experimental data is illustrated in Table 1. Calculated values of ΔH_f^0(g) for primary alkyl bromides (column 6) show near-perfect agreement with corresponding values (column 7) calculated by Skinner [4] using the bond-energy scheme. This illustrates the fact that, despite its speed and simplicity, the Displacement Rule method gives ΔH_f^0(g) values that are practically identical with values developed from the bond-energy scheme. (The bond-energy scheme is, of course, broader, applying also to secondary and tertiary alkyls, compounds with which this paper is not concerned.)

TABLE 1

COMPARISON OF CALCULATED VALUES OF $-\Delta H_f^0$(g) (kcal/gfw): DISPLACEMENT RULE VS. ALLEN SCHEME

Compound	R'	$-\Delta H_f^0$(g)[a] (obs.)	$-\Delta H_f^0[R'CH_3(g)]$[b]	$\Delta H_{Br(R')}$[c]	$-\Delta H_f^0$(g) (calcd.)	
					Displacement Rule[d]	Bond energy scheme[a]
MeBr	H	9.6	17.89	8.29	(9.84)[e]	9.85
EtBr	Me	15.3	20.24	4.94	16.19	16.20
PrBr	Et	21.1	25.17	4.07	21.12	21.13
BuBr	Pr	26.01	30.10	4.09	26.05	26.06
PeBr	Bu	31.13	35.03	3.90	30.98	30.99
HxBr	Pe	35.88	39.96	4.08	35.91	35.92
HpBr	Hx	40.69	44.89	4.20	40.84	40.85
OcBr	Hp	46.26	49.82	3.56	45.77	45.78
i-BuBr	i-Pr	28.4	32.15	3.75	28.10	28.09

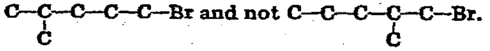
[a] As given by Skinner [4]. [b] From Table 2. [c] $\Delta H_{Br(R')} = \Delta H_f^0[R'CH_2Br(g)] - \Delta H_f^0[R'CH_3(g)]$.
[d] ΔH_f^0(g) (calcd.) = $\overline{\Delta H}_{Br(R)} + \Delta H_f^0[RCH_3(g)] \cdot \overline{\Delta H}_{Br(R)}$ was evaluated as 4.05 by averaging the last 8 values of $\Delta H_{Br(R')}$ (in getting this average, the numbers 4.94 and 3.56 were given only half weight).
[e] Calculated from $\Delta H_{Br(H)} = \overline{\Delta H}_{Br(R)} + \Gamma_{CCBr} = 4.05 + 4.00 = 8.05$; $\Delta H_f^0[HCH_2Br(g)] = \Delta H_{Br(H)} + \Delta H_f^0[HCH_3(g)] = 8.05 - 17.89 = -9.84$ using $\Gamma_{CCBr} = 4.00$ as recommended by Skinner (if, instead, the observed value of -9.6 is accepted, one calculates $\Gamma_{CCBr} = 4.24$).

TABLE 2

HEATS OF FORMATION[a] OF GASEOUS ALKANES (RH) USED IN APPLYING THE DISPLACEMENT RULE

Alkyl group (straight-chain)	$-\Delta H_f^0[\mathrm{RH(g)}]$	Alkyl group (iso-)[b]	$-\Delta H_f^0[\mathrm{RH(g)}]$
Me	17.89		
Et	20.24		
Pr	25.17		
Bu	30.10	i-Bu	32.15
Pe	35.03	i-Pe	36.92
Hx	39.96	i-Hx	41.66
Hp	44.89	i-Hp	46.59
Oc	49.82	i-Oc	51.52

[a] Observed values [6] except for propane, n-butane and n-pentane for which smoothed values are used.
[b] i-RH refers to the 2-Me compound. When an i-R group other than i-Bu is linked to an atom other than H, the linkage is understood to occur at the non-branched end of the group. Thus i-HxBr is



$\mathrm{C{-}\underset{\displaystyle C}{C}{-}C{-}C{-}C{-}Br}$ and not $\mathrm{C{-}C{-}C{-}\underset{\displaystyle C}{C}{-}C{-}Br}$.

Application to metal alkyls: The "Extended Displacement Rule for Metals"

Reliable heat of formation data on homologous series of metal alkyls are relatively scarce. Fortunately data are available on the boron alkyls from methyl through n-octyl while data from methyl through n-butyl (or n-propyl) are avail-

TABLE 3

CALCULATION OF $\Delta H_{\mathrm{X(R')}}$ VALUES FOR METAL PRIMARY ALKYLS FROM EXPERIMENTAL HEATS OF FORMATION

Compound[a]	R'[a]	Ref.	$\Delta H_f^0(\mathrm{l})$[b]	ΔH_v^0[c]	$\Delta H_f^0(\mathrm{g})$	$-\Delta H_f^0[\mathrm{R'CH_3(g)}]$[d]	$\Delta H_{\mathrm{X(R')}}$[e]
$\mathrm{Me_3B}$	H	7	− 33.9	4.8	− 29.1	17.89	24.6
$\mathrm{Me_3B}$	H	8	− 34.2	4.8	− 29.4	17.89	24.3
$\mathrm{Et_3B}$	Me	8	− 46.5	8.5	− 38.0	20.24	22.7
$\mathrm{Et_3B}$	Me	9	− 44.2	8.5	− 35.7	20.24	25.0
$\mathrm{Bu_3B}$	Pr	8	− 82.5	14.8	− 67.7	30.10	22.6
$\mathrm{Hx_3B}$	Pe	9	−116.0	21.2	− 94.8	39.96	25.1
$\mathrm{Hp_3B}$	Hx	9	−133.8	24.4	−109.4	44.89	25.8
$\mathrm{Oc_3B}$	Hp	9	−152.1	27.6	−124.5	49.82	25.0
$\mathrm{Me_2Zn}$	H	2	6.0	7.1	13.1	17.89	48.9
$\mathrm{Et_2Zn}$	Me	2	4.0	9.6	13.6	20.24	54.1
$\mathrm{Pr_2Zn}$	Et	7	− 13.8	10.9	− 2.9	25.17	47.4
$\mathrm{Bu_2Zn}$	Pr	7	− 24.9	13.0	− 11.9	30.10	48.3
$\mathrm{Me_2Hg}$	H	2	14.0	8.3	22.3	17.89	58.1
$\mathrm{Et_2Hg}$	Me	2	7.1	10.7	17.8	20.24	58.3
$\mathrm{Pr_2Hg}$	Et	2	− 5.0	13.2	8.2	25.17	58.5
$\mathrm{Me_4Sn}$	H	10	− 12.5	7.9	− 4.6	17.89	67.0
$\mathrm{Me_3EtSn}$	H, Me	10	− 16.1	9.0	− 7.1	17.89, 20.24	66.8
$\mathrm{Et_4Sn}$	Me	10	− 22.9	12.2	− 10.7	20.24	70.3
$\mathrm{Pr_4Sn}$	Et	10	− 50.5	16.0	− 34.5	25.17	66.2
$\mathrm{Bu_4Sn}$	Pr	10	− 72.8	19.8	− 53.0	30.10	67.4
$\mathrm{i\text{-}Bu_4Sn}$	i-Pr	11	− 79.1	18.7	− 60.4	32.15	68.2

[a] In this table and in succeeding tables, "Pr" means n-Pr, "$\mathrm{Bu_3B}$" means $\mathrm{(n\text{-}Bu)_3B}$, etc. [b] Recalculated from original heats of reaction using most recent ΔH_f^0 for components. [c] Essentially as given by Cox and Pilcher [2]. [d] From Table 2. [e] $\Delta H_{\mathrm{X(R')}} = \Delta H_f^0[\mathrm{(R'CH_2)_mX(M,\,g)}] - m\Delta H_f^0[\mathrm{R'CH_3(g)}]$.

able for zinc, mercury and tin. The experimental values of $\Delta H_f^0(l)$ for these alkyls are listed in column 4 of Table 3. Values of $\Delta H_{X(R')}$ calculated therefrom are shown in column 7. For each of these elements, according to the Displacement Rule, the values of $\Delta H_{X(R')}$ for the alkyls above methyl should all be the same so that differences among them reflect experimental error. In each case, $\Delta H_{X(R')}$ for the methyl compound agrees closely (well within experimental error) with the weighted average of the values for the higher alkyls. It is therefore reasonable to regard the Displacement Rule as being extended to include the methyl compound (R′ = H or R) for each of these elements. Weighted averages $\overline{\Delta H}_{X(R')}$, based on all the $\Delta H_{X(R')}$ values, were determined as follows: 24.3 for boron, 48.8 for zinc, 58.3 for mercury, and 67.1 for tin.

Best values of $\Delta H_f^0(g)$ for boron primary alkyls, calculated from eqn. 3 (with R′ allowed to be either H or any alkyl group) or from eqn. 7 (modified to accommodate a trivalent element) are listed in column 3 of Table 4. Calculated values of $\Delta H_f^0(l)$ (column 4) show good agreement with experimental values (column 5).

Calculated values of $\Delta H_f^0(g)$ and $\Delta H_f^0(l)$ for primary alkyls of zinc, mercury and tin are presented similarly in Tables 5, 6 and 7. In each instance, the

TABLE 4

CALCULATED VALUES OF $-\Delta H_f^0(g)$ AND $-\Delta H_f^0(l)$ FOR BORON PRIMARY ALKYLS BASED ON $\overline{\Delta H}_{B(R')} = 24.3$

Compound	ΔH_v^{0a}	Calculated values		Experimental values of $-\Delta H_f^0(l)$
		$-\Delta H_f^0(g)^b$	$-\Delta H_f^0(l)^c$	-
Me_3B	4.8	29.4	34.2	33.9[d], 34.2[e]
Et_3B	8.5	36.4	44.9	46.5[e], 44.2[f]
Pr_3B	11.6	51.2	62.8	
Bu_3B	14.8	66.0	80.8	82.5[e]
Pe_3B	18.0	80.8	98.8	
Hx_3B	21.2	95.6	116.8	116.0[f]
Hp_3B	24.4	110.4	134.8	133.8[f]
Oc_3B	27.6	125.1	152.7	152.1[f]
[Increment][g]	[3.2]	[14.8]	[18.0]	
Me_2EtB	6.2	31.7	37.9	
$MeEt_2B$	7.3	34.1	41.4	
$MeBu_2B$	12.0	53.8	65.8	
MeEtPrB	8.5	39.0	47.5	
$i\text{-}BuBMe_2$	7.9	43.6	51.5	
$i\text{-}BuBEt_2$	10.2	48.3	58.5	
$i\text{-}Pe_3B$[h]	17.1	86.5	103.6	
$i\text{-}Hx_3B$[h]	20.4	100.7	121.1	
$i\text{-}Hp_3B$[h]	23.7	115.5	139.2	
$i\text{-}Oc_3B$[h]	27.0	130.3	157.3	
[Increment][g]	[3.3]	[14.8]	[18.1]	

[a] Values not taken from Table 3 were estimated (estimated uncertainties range from ±0.2 for Me_3B to ±1.4 for Oc_3B. [b] Estimated uncertainty: ±1.8. [c] Estimated uncertainties: from ±1.8 for Me_3B to ±2.3 for Oc_3B. Uncertainties were combined by summing their squares and extracting the square root. [d] Ref. 7. [e] Ref. 8. [f] Ref. 9. [g] Increment per unit increase in carbon no. of R-group for obtaining values for higher homologs. [h] It is assumed that there are no steric effects present in the molecule since branching is remote from the boron atom.

TABLE 5

CALCULATED VALUES OF $\Delta H_f^0(g)$ AND $\Delta H_f^0(l)$ FOR ZINC PRIMARY ALKYLS BASED ON $\overline{\Delta H}_{Zn(R')} = 48.8$

Compound	ΔH_v^0[a]	Calculated values		Experimental values of $\Delta H_f^0(l)$
		$\Delta H_f^0(g)$[b]	$\Delta H_f^0(l)$[c]	
Me_2Zn	7.1	13.0	5.9	6.0[d]
Et_2Zn	9.6	8.3	− 1.3	4.0[d]
Pr_2Zn	10.9	− 1.5	−12.4	−13.8[e]
Bu_2Zn	13.0	−11.4	−24.4	−24.9[e]
[Increment]	[2.4]	$[-9.8_6]$	$[-12.2_6]$	
MeEtZn	8.3	10.7	2.4	
MePrZn	9.6	5.7	− 3.9	
EtBuZn	10.9	− 1.5	−12.4	
$i\text{-}Bu_2Zn$	12.3	−15.5	−27.8	
$i\text{-}Pe_2Zn$	14.7	−25.0	−39.7	
$i\text{-}Hx_2Zn$	17.1	−34.5	−51.6	
[Increment]	[2.4]	$[-9.8_6]$	$[-12.2_6]$	

[a] Values not taken from Table 3 were estimated (estimated uncertainties: from ±0.2 for Me_2Zn to ±0.9 for $i\text{-}Hx_2Zn$). [b] Estimated uncertainty: ±2.7. [c] Estimated uncertainties: from ±2.7 for Me_2Zn to ±2.8 for $i\text{-}Hx_2Zn$. [d] Ref. 2. [e] Ref. 7.

agreement between calculated and experimental values of $\Delta H_f^0(l)$ is satisfactory.

Since $\Delta H_{X(H)} \approx \Delta H_{X(R)}$ for boron, zinc, mercury and tin, it follows that $\Gamma_{CCX} \approx 0$ for each of these metals. The average bond dissociation energies of

TABLE 6

CALCULATED VALUES OF $\Delta H_f^0(g)$ AND $\Delta H_f^0(l)$ FOR MERCURY PRIMARY ALKYLS BASED ON $\overline{\Delta H}_{Hg(R')} = 58.3$.

Compound	ΔH_v^0[a]	Calculated values		Experimental values of $\Delta H_f^0(l)$
		$\Delta H_f^0(g)$[b]	$\Delta H_f^0(l)$[c]	
Me_2Hg	8.3	22.5	14.2	14.0[d]
Et_2Hg	10.7	17.8	7.1	7.1[d]
Pr_2Hg	13.2	8.0	− 5.2	− 5.0[d]
Bu_2Hg	15.6	− 1.9	−17.5	
[Increment]	[2.4]	$[-9.8_6]$	$[-12.2_6]$	
MeEtHg	9.5	20.2	10.7	
MePrHg	10.7	15.2	4.5	
EtBuHg	13.2	8.0	− 5.2	
$i\text{-}Bu_2Hg$	14.9	− 6.0	−20.9	
$i\text{-}Pe_2Hg$	17.3	−15.5	−32.8	
$i\text{-}Hx_2Hg$	19.7	−25.0	−44.7	
[Increment]	[2.4]	$[-9.8_6]$	$[-12.2_6]$	

[a] Values not taken from Table 3 were estimated (estimated uncertainties: from ±0.2 for Me_2Hg to ±1.0 for $i\text{-}Hx_2Hg$). [b] Estimated uncertainty: ±0.5. [c] Estimated uncertainties: from ±0.5 for Me_2Hg to ±1.1 for $i\text{-}Hx_2Hg$. [d] Ref. 2.

TABLE 7

CALCULATED VALUES OF $-\Delta H_f^0(g)$ AND $-\Delta H_f^0(l)$ FOR TIN PRIMARY ALKYLS BASED ON $\overline{\Delta H}_{Sn(R')} = 67.1$

Compound	ΔH_v^0[a]	Calculated values		Experimental values of $-\Delta H_f^0(l)$
		$-\Delta H_f^0(g)$[b]	$-\Delta H_f^0(l)$[c]	
Me_4Sn	7.9	4.5	12.4	12.5[d]
Et_4Sn	12.2	13.9	26.1	22.9[d]
Pr_4Sn	16.0	33.6	49.6	50.5[d]
Bu_4Sn	19.8	53.3	73.1	72.8[d]
[Increment]	[3.8]	[19.7]	[23.5]	
Me_3EtSn	9.0	6.8	15.8	16.1[d]
Me_2Et_2Sn	10.0	9.2	19.2	
$MeEt_3Sn$	11.1	11.5	22.6	
MeEtPrBuSn	14.0	26.3	40.3	
i-Bu_4Sn	18.7	61.5	80.2	79.1[e]
i-Pe_4Sn	22.6	80.6	103.2	
i-Hx_4Sn	26.5	99.5	126.0	
[Increment]	[3.9]	[19.7]	[23.6]	

[a] Values not taken from Table 3 were estimated (estimated uncertainties: from ±0.2 for Me_4Sn to ±1.3 for i-Hx_4Sn). [b] Estimated uncertainty: ±1.7. [c] Estimated uncertainties: from ±1.7 for Me_4Sn to ±2.1 for i-Hx_4Sn. [d] Ref. 10. [e] Ref. 11.

the methyl compounds of these metals, $\bar{D}(X{-}Me)$*, cover a broad range: 88 for boron, 53 for tin, 43 for zinc and 30 kcal for mercury. The following related metals have $\bar{D}(X{-}Me)$ values which fall within this range: Al($\bar{D}$ = 67), Ga(61), In(≈52), Tl(≈36), Ge(62), Pb(37), Cd(34), Sb(49), and Bi(35). Pending the availability of reliable thermochemical data on the alkyls of these metals, it is reasonable to assume that $\Gamma_{CCX} = 0$** and therefore $\Delta H_{X(H)} = \Delta H_{X(R)}$**, for each metal. In other words, it is assumed that each of these nine metals, along with B, Zn, Hg and Sn, obey the "Extended Displacement Rule for Metals."

Heats of formation of aluminum alkyls

The experimental values of $\Delta H_f^0(l)$ for aluminum trialkyls are listed in column 3 of Table 8. Corresponding values of ΔH_f^0 for the gaseous monomers are given in column 7. Values of $\Delta H_{Al(R')}$ calculated therefrom (last column) range from 18.9 to 42.4 kcal. Of the three values for Me_3Al, the high one (40.1) is rejected since it deviates so far from the average of all the values (29.8). The other two values for Me_3Al (32.8 and 32.5) agree closely. The value 32.8, corresponding to the measurements of Mortimer and Sellers [17],

---

* Values of $\bar{D}(X{-}Me)$ were calculated as $\Delta H_r/m$ where m = no. of Me groups per (monomeric) molecule and $\Delta H_r = \Delta H$ of the reaction $Me_mX(g) \rightarrow m Me(g) + X(g)$. Current ΔH_f^0 values were used for $Me_mX(g)$. Values of ΔH_f^0 for X(g) and Me(g) (34.0 ± 1.0 kcal) are from ref. 2. The values of $\bar{D}(X{-}Me)$ listed for In and Tl were estimated from a "periodic array" of the values for the other elements (the value of 40 for In calculated from experimental data [2], while not necessarily incorrect, was not used since it appears to be too small in comparison with the values for the neighboring elements).

** Estimated uncertainty ±0.5.

TABLE 8

CALCULATION OF $\Delta H_{Al(R')}$ VALUES FROM EXPERIMENTAL HEATS OF FORMATION OF LIQUID ALUMINUM TRIALKYLS

Ref.	Compound	$-\Delta H_f^0(l)^a$	$\Delta H_d^{0\,b}$	$-\Delta H_f^0(M,l)$	$\Delta H_v^0(M)^c$	$-\Delta H_f^0(M,g)$	$-\Delta H_f^0[R'CH_3(g)]^d$	$\Delta H_{Al(R')}{}^e$
7	Me_3Al	28.7	9.7^f	19.0	5.4	13.6	17.89	40.1
17	Me_3Al	36.0	9.7^f	26.3	5.4	20.9	17.89	32.8
16	Et_3Al	37.5	8.5^g	29.0	9.5	19.5	20.24	41.2
18	Et_3Al	41.4	8.5^g	32.9	9.5	23.4	20.24	37.3
19	Me_3Al	36.3	9.7^f	26.6	5.4	21.2	17.89	32.5
20	Et_3Al	51.9	8.5^g	43.4	9.5	33.9	20.24	26.8
21	Pr_3Al	68.5	7.7^h	60.8	12.7	48.1	25.17	27.4
22	i-Bu_3Al	69.9	1.1^i	68.8	14.9	53.9	32.15	42.5
23	Et_3Al	56.6	8.5^g	48.1	9.5	38.6	20.24	22.1
23	Pr_3Al	77.0	7.7^h	69.3	12.7	56.6	25.17	18.9
23	Bu_3Al	89.0	7.4^h	81.6	15.9	65.7	30.10	24.6
23	i-Bu_3Al	92.8	1.1^i	91.7	14.9	76.8	32.15	19.6

[a] Recalculated from original heats of reaction using most recent values of ΔH_f^0 for components. [b] ΔH_f^0 of equilibrium mixture of monomer and dimer. [c] Value for Me_3Al is from ref. 14. Other values were estimated. [d] From Table 2. [e] $\Delta H_{Al(R')} = \Delta H_f^0[(R'CH_2)_3Al(M,g)] - 3\Delta H_f^0[R'CH_3(g)]$ [f] Ref. 14. [g] Ref. 12. [h] Ref. 15. [i] Ref. 13.

appears to be the most reliable single value in the table (the measured heat of reaction was much smaller than the heats of combustion determined by most of the other investigators and therefore less subject to error). Since it is also reasonably close to the average of all the values, 32.8 was selected somewhat arbitrarily as the best value for $\Delta H_{\mathrm{Al(R')}}$.

Values of ΔH_f^0(M, g) for aluminum alkyls were calculated via the Extended Displacement Rule for Metals using $\Delta H_{\mathrm{Al(R)}} = \Delta H_{\mathrm{Al(H)}} = 32.8$. These are listed in column 4 of Table 9. Calculated values of ΔH_f^0(l) (column 6) are compared with observed values (column 7). The calculated value for Me_3Al (—36.0), of course, matches the middle experimental value upon which the calculation was based. The calculated value for Et_3Al (—45.9) occupies a median position between the four observed values and, in fact, is quite close to the average of the four values (—46.8). Although the calculated values for Pr_3Al and Bu_3Al are lower in magnitude than the observed values, the calculated value for i-Bu_3Al (—79.5) falls between the two observed values. On the whole, this comparison between calculated and observed values tends to support the choice of $\Delta H_{\mathrm{Al(R')}} = 32.8$ and the use of the approximation $\Delta H_{\mathrm{Al(H)}} = \Delta H_{\mathrm{Al(R)}}$. It is perhaps worth mentioning that the value selected for ΔH_f^0 [Me_3Al(M, g)], —20.9, occupies a reasonable position between corresponding values for Me_3B (—29.4) and Me_3Ga (—11.2).

TABLE 9

CALCULATED VALUES OF $-\Delta H_f^0$(M, g), $-\Delta H_f^0$(M, l) AND $-\Delta H_f^0$(l) FOR ALUMINUM PRIMARY ALKYLS BASED ON $\Delta H_{\mathrm{Al(H)}} = \Delta H_{\mathrm{Al(R)}} = 32.8$

Compound[a]	ΔH_v^0(M)[b]	ΔH_d^0(l)	Calculated values			Experimental values of $-\Delta H_f^0$(l)
			$-\Delta H_f^0$(M, g)[c]	$-\Delta H_f^0$(M, l)[d]	$-\Delta H_f^0$(l)[e]	
Me_3Al	5.4	9.7[f]	20.9	26.3	36.0	28.7[g], 36.0[h], 36.3[i]
Et_3Al	9.5	8.5[j]	27.9	37.4	45.9	37.5[k], 41.4[l], 51.9[m], 56.6[n]
Pr_3Al	12.7	7.7[o]	42.7	55.4	63.1	68.5[p], 77.0[n]
Bu_3Al	15.9	7.4[o]	57.5	73.4	80.8	89.0[n]
Pe_3Al	19.1	7.3[o]	72.3	91.4	98.7	
Hx_3Al	22.3	7.3[o]	87.1	109.4	116.7	
Hp_3Al	25.5	7.3[o]	101.9	127.4	134.7	
Oc_3Al	28.7	7.2[o]	116.7	145.4	152.6	
[Increment]	[3.2]	[0.0]	[14.8]	[18.0]	[18.0]	
i-Bu_3Al	14.9	1.1[g]	63.6	78.5	79.6	69.9[r], 92.8[n]
i-Pe_3Al	18.2	(7.0)[o]	78.0	96.2	(103.2)	
i-Hx_3Al	21.5	7.3[o]	92.2	113.7	121.0	
i-Hp_3Al	24.8	7.3[o]	107.0	131.8	139.1	
i-Oc_3Al	28.1	7.2[o]	121.8	149.9	157.1	
[Increment]	[3.3]	[0.0]	[14.8]	[18.1]	[18.1]	

[a] For the iso-compounds other than i-Bu_3Al, the point of attachment of the i-R group to the Al atom is remote from the (single methyl) branching.
[b] Value for Me_3Al is from ref. 14. Other values were estimated. Estimated uncertainties: from ±0.2 for Me_3Al to ±1.4 for Oc_3Al.
[c] $\Delta H_f^0(\mathrm{M, g}) = 32.8 + 3\Delta H_f^0[\mathrm{RH(g)}]$. Estimated uncertainties: ±1.7 for Me_3Al, ±2.2 for all other compounds.
[d] $\Delta H_f^0(\mathrm{M, l}) = \Delta H_f^0(\mathrm{M, g}) - \Delta H_v^0(\mathrm{M})$. Estimated uncertainties: from ±1.6 for Me_3Al to ±2.6 for Oc_3Al.
[e] $\Delta H_f^0(\mathrm{l}) = \Delta H_f^0(\mathrm{M, l}) - \Delta H_d^0(\mathrm{l})$. Estimated uncertainties: from ±1.6 for Me_3Al to ±2.6 for Oc_3Al. This is ΔH_f^0 for the "real liquid" (equilibrium mixture of monomer and dimer). It is indistinguishable from ΔH_f^0(D, l) for Me_3Al, Et_3Al and Pr_3Al but is slightly lower in magnitude than ΔH_f^0(D, l) for the higher alkyls.
[f] Ref. 14. [g] Ref. 7. [h] Ref. 17. [i] Ref. 19. [j] Ref. 12. [k] Ref. 16. [l] Ref. 18. [m] Ref. 20. [n] Ref. 23. [o] Ref. 15. [p] Ref. 21. [q] Ref. 13. [r] Ref. 22.

In applying the Extended Displacement Rule for Metals to (monomeric) aluminum alkyls, we have, in effect, given Γ_{CCAl} the value zero. In a 1964 survey, Skinner [24] recommended the value −3.0. This was derived from "selected values" of −36.0 for $\Delta H_f^0[\mathrm{Me_3Al(l)}]$ (also selected in the present study) and −36.5 for $\Delta H_f^0[\mathrm{Et_3Al(l)}]$ (since updated to −37.5). Since the three larger values for $\mathrm{Et_3Al}$ (−41.4, −51.9 and −56.6) have all appeared subsequent to Skinner's survey, it is no longer reasonable to accept −37.5 as the "best value" for $\mathrm{Et_3Al}$. Hence, the value of −3.0 for Γ_{CCAl} must be rejected.

In their 1970 book, Cox and Pilcher [2] have also selected −36.0 for $\Delta H_f^0[\mathrm{Me_3Al(l)}]$ but have selected −56.6 for $\Delta H_f^0[\mathrm{Et_3Al(l)}]$. From these values, one can calculate Γ_{CCAl} from eqn. 5 as $\frac{1}{3}(32.8-22.1) = +3.6$. [Cox and Pilcher (p. 594) also recommend $\Gamma_{\mathrm{CCAl}} = -3.0$; apparently they overlooked the need to update the value recommended by Skinner.] This value of +3.6 for Γ_{CCAl} is very unlikely to be correct since such large positive values are characteristic of the strongly electronegative elements but not of the metals. This is further confirmation of the fact that the value of −56.6 for $\Delta H_f^0[\mathrm{Et_3Al(l)}]$ is, in all likelihood, thermodynamically inconsistent with the value of −36.0 for $\Delta H_f^0[\mathrm{Me_3Al(l)}]$.

Heats of formation of the dialkylaluminum hydrides

The equation for the heats of formation of the dialkylaluminum hydrides was derived by application of the Extended Displacement Rule for Metals:

$$\mathrm{Al(c)} + 2\mathrm{R'CH_3(g)} \rightarrow \mathrm{(R'CH_2)_2AlH(M,\,g)} + \mathrm{H_2(g)}$$

$$\Delta H = \text{constant} = \Delta H_{\mathrm{AlH(R')}} = \Delta H_f^0[\mathrm{(R'CH_2)_2AlH(M,\,g)}] - 2\Delta H_f^0[\mathrm{R'CH_3(M,\,g)}]$$

where R′ is any alkyl group or hydrogen. Substituting R for $\mathrm{R'CH_2}$, we obtain:

$$\Delta H_f^0[\mathrm{R_2AlH(M,\,g)}] = \Delta H_{\mathrm{AlH(R')}} + 2\Delta H_f^0[\mathrm{RH(g)}]$$

$$\Delta H_f^0[\mathrm{R_2AlH(M,\,l)}] = \Delta H_f^0[\mathrm{R_2AlH(M,\,g)}] - \Delta H_v^0(\mathrm{M})$$

$$\Delta H_f^0[\mathrm{R_2AlH\,(l)}] = \Delta H_f^0[\mathrm{R_2AlH(T,\,l)}] = \Delta H_f^0[\mathrm{R_2AlH(M,\,l)}] - \Delta H_d^0(\mathrm{l})$$

The value of $\Delta H_d^0(\mathrm{l})$ was estimated as 16.5 ± 2.0 kcal/gfw from heat-of-complexation measurements on $\mathrm{Me_2AlH}$ [25], $\mathrm{Et_2AlH}$ [25] and i-$\mathrm{Bu_2AlH}$ [26]. This value, assumed to apply to all the dialkylaluminum hydrides, agrees well with the figure given by Coates [27] (17.5 ± 2.5 kcal/gfw).

In order to evaluate the constant $\Delta H_{\mathrm{AlH(R')}}$, it is helpful to consider the hydrogenolysis reaction (eqns. 8 and 9). Values of $\Delta H_{\mathrm{hy.}}(\mathrm{M,\,g})$ were calculated from Pawlenko's [23] experimental data on $\mathrm{R_2AlH}$ and $\mathrm{R_3Al}$ using eqn. 8. These are listed in Table 10. The lone positive value of $\Delta H_{\mathrm{hy.}}(\mathrm{M,\,g})$ was disregarded. (From consideration of the bond energies involved in the hydrogenolysis reaction, it seems likely that the reaction is not endothermic.) The average

$$\mathrm{R_3Al(M,\,g)} + \mathrm{H_2(g)} \rightarrow \mathrm{R_2AlH(M,\,g)} + \mathrm{RH(g)}$$

$$\begin{aligned}\Delta H = \Delta H_{\mathrm{hy.}}(\mathrm{M,\,g}) &= \Delta H_f^0[\mathrm{R_2AlH(M,\,g)}] + \Delta H_f^0[\mathrm{RH(g)}] - \Delta H_f^0[\mathrm{R_3Al(M,\,g)}] \qquad (8)\\ &= \Delta H_{\mathrm{AlH(R')}} + 2\Delta H_f^0[\mathrm{RH(g)}] + \Delta H_f^0[\mathrm{RH(g)}] - 32.8\\ &\quad - 3\Delta H_f^0[\mathrm{RH(g)}]\end{aligned}$$

TABLE 10

CALCULATION OF $\Delta H_{\text{hy.}}$ (M, g) FROM EXPERIMENTAL DATA

R	$-\Delta H_f^0[R_2AlH(T, l)]$[a]	$\Delta H_v^0(M)$[b]	$-\Delta H_f^0[R_2AlH(M, g)]$[c]	$-\Delta H_f^0[R_3Al(M, g)]$[d]	$\Delta H_{\text{hy.}}(M, g)$[e]
Et	48.7	7.4	24.8	38.6	−6.4
Pr	58.1	9.8	31.8	56.6	−0.4
Bu	67.6	12.1	39.0	65.7	−3.4
i-Bu	69.1	11.4	41.2	76.8	+3.4

[a] Experimental values [23]. [b] Estimated. [c] $\Delta H_f^0[R_2AlH(M, g)] = \Delta H_f^0[R_2AlH(T, l)] + 16.5 + \Delta H_v^0(M)$. [d] From Table 8 (Pawlenko). [e] Calculated from eqn. 8.

$$\Delta H_{\text{hy.}}(M, g) = \Delta H_{AlH(R')} - 32.8 = \text{a constant} \tag{9}$$

of the three negative values, $\overline{\Delta H}_{\text{hy.}}(M, g) = -3.4^*$, leads to $\Delta H_{AlH(R')} = -3.4 + 32.8 = 29.4$.

The derived value, $\Delta H_{AlH(R')} = 29.4$, can be tested by means of the redistribution reaction (eqn. 10). $\Delta H^0_{\text{red.}}$ (M, g) was estimated as −1.5 ± 0.5 from

$$\tfrac{1}{3}AlH_3(M, g) + \tfrac{2}{3}R_3Al(M, g) \rightarrow R_2AlH(M, g)$$

$$\begin{aligned}\Delta H = \Delta H^0_{\text{red.}}(M, g) &= \Delta H_{AlH(R')} + 2\,\Delta H_f^0[RH(g)] - \tfrac{1}{3}\Delta H_f^0[AlH_3(M, g)] \\ &\quad - \tfrac{2}{3}(32.8) - 2\,\Delta H_f^0[RH(g)] \\ &= \Delta H_{AlH(R')} - \tfrac{1}{3}\Delta H_f^0[AlH_3(M, g)] - 21.9\end{aligned}$$

$$\Delta H_f^0[AlH_3(M, g)] = 3[\Delta H_{AlH(R')} - 21.9 - \Delta H^0_{\text{red.}}(M, g)] \tag{10}$$

data** on related redistribution reactions. Substituting in eqn. 10, the value of $\Delta H_f^0[AlH_3(M, g)]$ corresponding to $\Delta H_{AlH(R')} = 29.4$ is calculated as 27.0 ± 6.0. This value appears reasonable when compared to the accepted value of 24 [28] for $BH_3(M, g)$ and thus supports the value of 29.4 for $\Delta H_{AlH(R')}$. The mean bond dissociation energy was calculated from $\Delta H_f^0[AlH_3(M, g)] = 27.0$ as $\bar{D}(Al{-}H) = 69.1$ kcal. This is 2.1 kcal greater than $\bar{D}(Al{-}Me)$ which was calculated from $\Delta H_f^0[Me_3Al(M, g)]$ as 67.0 kcal. This is reasonable since $\bar{D}(X{-}H)$ is at least 7 kcal larger than $\bar{D}(X{-}Me)$ for each element belonging to Group IVA or VA of the periodic system, while $D(X{-}H) \approx D(X{-}Me)$ for boron. The value $\Delta H_{AlH(R')} = 29.4$ is therefore also consistent with bond energy relationships.

The equations for the dialkylaluminum hydrides thus become:

$$\Delta H_f^0[R_2AlH(M, g)] = 29.4 + 2\,\Delta H_f^0[RH(g)] \tag{11}$$

$$\Delta H_f^0[R_2AlH(M, l)] = \Delta H_f^0[R_2AlH(M, g)] - \Delta H_v^0(M) \tag{12}$$

$$\Delta H_f^0[R_2AlH(T, l)] = \Delta H_f^0[R_2AlH(M, l)] - 16.5 \tag{13}$$

---

* Estimated uncertainty ±2.0.

** For $\tfrac{1}{4}SnH_4(g) + \tfrac{3}{4}R_4Sn(g) \rightarrow R_3SnH(g)$, $\Delta H^0_{\text{red.}} \approx -2.5$ (data of Stack et al. [29] for R = Pr, Bu after converting to gas phase). For $\tfrac{1}{4}SnCl_4(g) + \tfrac{3}{4}R_4Sn(g) \rightarrow R_3SnCl(g)$, $\Delta H^0_{\text{red.}} \approx -8.0$ (liquid phase equation given by Stack et al. [29] for R = Et was converted to gas phase). For $\tfrac{1}{3}AlCl_3(M, g) + \tfrac{2}{3}R_3Al(M, g) \rightarrow R_2AlCl(M, g)$, $\Delta H^0_{\text{red.}} \approx -4.7$ (estimated from data given in this paper). Assuming $\Delta H^0_{\text{red.}}(H)/\Delta H^0_{\text{red.}}(Cl)$ to have the same value for Al as for Sn (0.31), $\Delta H^0_{\text{red.}}(H)$ for Al is calculated as −1.5 kcal.

TABLE 11

HEATS OF FORMATION OF DIALKYLALUMINUM HYDRIDES

Compound[a]	$\Delta H_v^0(M)$[b]	Calculated values			$-\Delta H_f^0(T, l)$, Exptl.	
		$-\Delta H_f^0(M, g)$[c]	$-\Delta H_f^0(M, l)$[d]	$-\Delta H_f^0(T, l)$[e]	Pawlenko[f]	Shaulov[g]
Me_2AlH	4.4	6.4	10.8	27.3		
Et_2AlH	7.4	11.1	18.5	35.0	48.7	73.5
Pr_2AlH	9.8	21.0	30.7	47.2	58.1	
Bu_2AlH	12.1	30.8	42.9	59.4	67.6	
Pe_2AlH	14.5	40.7	55.2	71.7		
Hx_2AlH	16.9	50.5	67.4	83.9		
Hp_2AlH	19.2	60.4	79.6	96.1		
Oc_2AlH	21.6	70.3	91.9	108.4		
[Increment]	[2.3_6]	[9.8_6]	[12.2]	[12.2]		
i-Bu_2AlH	11.4	34.9	46.3	62.8	69.1	96.1
i-Pe_2AlH	13.8	44.5	58.3	74.8		
i-Hx_2AlH	16.2	53.9	70.1	86.6		
i-Hp_2AlH	18.6	63.8	82.4	98.9		
i-Oc_2AlH	21.0	73.7	94.7	111.2		
[Increment]	[2.4_2]	[9.8_6]	[12.3]	[12.3]		

[a] For the iso-compounds other than i-Bu_2AlH, the point of attachment of the i-R group to the Al atom is remote from the (single methyl) branching. [b] Estimated. (Estimated uncertainties: from ± 0.2 for Me_2AlH to ± 1.1 for Oc_2AlH). [c] $\Delta H_f^0(M, g) = 29.4 + 2\,\Delta H_f^0[RH(g)]$. (Estimated uncertainties ± 3.0). [d] $\Delta H_f^0(M, l) = \Delta H_f^0(M, g) - \Delta H_v^0(M)$. (Estimated uncertainties: from ± 3.0 for Me_2AlH to ± 3.2 for Oc_2AlH). [e] $\Delta H_f^0(T, l) = \Delta H_f^0(M, l) - 16.5$. (Estimated uncertainties: from ± 3.6 for Me_2AlH to ± 3.8 for Oc_2AlH). [f] Ref. 23. [g] Ref. 20.

Heats of formation calculated from these equations are listed in Table 11. Calculated values of $\Delta H_f^0(l)$ in column 5 are compared with experimental values in column 6. The observed values reported by Shaulov [20] are far too large in magnitude to merit serious consideration. As was the case with R_3Al, observed values of Pawlenko [23] for R_2AlH are ≈10 kcal larger in magnitude than the corresponding calculated values. As was shown previously, these high values are thermodynamically inconsistent with the selected value of —36.0 for $\Delta H_f^0[Me_3Al(l)]$. It is therefore recommended that the calculated values of $\Delta H_f^0(l)$ for the dialkylaluminum hydrides be used in preference to the observed values.

Heat of hydrogenolysis of R_3Al

It was shown earlier that the heat of the hydrogenolysis reaction is a constant for the monomeric gaseous state and $\Delta H_{hy.}(M, g)$ was estimated as —3.4 kcal. Calculated values of $\Delta H_{hy.}(D \text{ or } T, l)$ for several different R-groups are listed in Table 12. The liquid state reactions are distinctly exothermic, particularly for R = i-Bu. This is consistent with experience since the reactions are known to proceed readily using pressurized hydrogen at 150—200° [27].

Heat of addition of olefin to R_2AlH

The addition of olefin to a dialkylaluminum hydride to form the corresponding aluminum trialkyl is represented by the equation:

$$R_2AlH + [Olef._R](g) \rightarrow R_3Al$$

$$\Delta H = \Delta H_{A.O.}$$

TABLE 12

HEAT OF HYDROGENOLYSIS[a] OF R_3Al

R	$-\Delta H_{hy.}$	
	(M, g)	(D or T, l)
Me	3.4	9.2
Et	3.4	9.3
Pr	3.4	9.3
Bu	3.4	8.7
Pe	3.4	8.0
Hx	3.4	7.2
i-Bu	3.4	15.3
i-Pe	3.4	8.5
i-Hx	3.4	7.3

[a] $R_3Al + H_2(g) \rightarrow R_2AlH + RH(g)$.

Calculated values of $\Delta H_{A.O.}$ (M, g) are compared in Table 13 with corresponding values, $\Delta H_{A.O.}(H_2)$, for the addition of olefin to hydrogen. The monomeric gas-phase addition of olefin to R_2AlH is 3.4 kcal less exothermic than the addition of olefin to hydrogen [this follows from $\Delta H_{hy.}$ (M, g) = —3.4]. Calculated values of $\Delta H_{A.O.}$(l) are compared with the observed values given by Pawlenko [23]. The agreement is fairly good for Et, Pr and Bu. The observed value for i-Bu, however, is inconsistent with the other observed values, being about 7 kcal too large in magnitude.

Larikov et al. [30] studied the thermal decomposition of liquid i-Bu_3Al into liquid i-Bu_2AlH and isobutylene over the range 55—129°. They calculated the ΔH for the reaction as 15.75 kcal/gfw from the temperature variation of the equilibrium constant. However, i-Bu_2AlH does not exist entirely as the trimer in mixtures with i-Bu_3Al (when it is first formed in dilute i-Bu_3Al solution, i-Bu_2AlH exists almost entirely as the co-dimer, i-Bu_2AlH·i-Bu_3Al [31]).

TABLE 13

HEAT OF ADDITION OF OLEFIN TO R_2AlH[a]

R	$-\Delta H_{A.O.}$(M, g)	$-\Delta H_{A.O.}(H_2)$[b]	$-\Delta H_{A.O.}$(l)	
			Calcd.	Obs.[c]
Et	29.3	32.7	23.4	20.3
Pr	26.6	30.0	20.8	23.7
Bu	26.6	30.0	21.4	21.4
Pe	26.6	30.0	22.0	
Hx	26.6	30.0	22.8	
i-Bu	24.7	28.1	12.8	19.6
i-Pe	26.6	30.0	21.5	
i-Hx	26.6	30.0	22.7	

[a] $R_2AlH + [Olef._R](g) \rightarrow R_3Al$. (The olefins considered are all primary olefins except for R = i-Bu).
[b] $-\Delta H$ of reaction: $H_2(g) + [Olef._R](g) \rightarrow RH(g)$. [c] Ref. 23.

Hence, the value of $\Delta H_{\text{A.O.}}$(l) for i-Bu cannot be determined in a clearcut fashion from these measurements.

Alkylaluminum dihydrides

The heat of formation of $RAlH_2$(M, g) may be calculated from the following redistribution reaction ($\Delta H^0_{\text{red.}}$ was estimated* as —1.5 ± 0.5):

$$\tfrac{2}{3}AlH_3(M, g) + \tfrac{1}{3}R_3Al(M, g) \rightarrow RAlH_2(M, g)$$

$$\Delta H = \Delta H^0_{\text{red.}}(M, g) = -1.5 = \Delta H^0_f[RAlH_2(M, g)] - \tfrac{2}{3}(27.0) - \tfrac{1}{3}(32.8)$$
$$- \Delta H^0_f[RH(g)]$$

$$\Delta H^0_f[RAlH_2(M, g)] = 27.4 + \Delta H^0_f[RH(g)]$$

(For R = Et, $\Delta H^0_f[EtAlH_2(M, g)] = 27.4 - 20.2 = 7.2$)

Using $\Delta H^0_v = 5.0$ (estimated) and $\Delta H^0_d(l) = 16.5$, $\Delta H^0_f[EtAlH_2(T, l)]$ is calculated as —14.3. The equation for the disproportionation of $EtAlH_2$(T, l) is:

$$EtAlH_2(T, l) \rightarrow \tfrac{1}{2}AlH_3(c) + \tfrac{1}{2}Et_2AlH(T, l)$$

Using —11.0 [28] for $\Delta H^0_f[AlH_3(c)]$, ΔH for the reaction is calculated as —8.7 kcal. Since ΔS for the reaction is relatively small in magnitude (although negative in sign), ΔF is large and negative. This indicates that $EtAlH_2$(T, l) is thermodynamically unstable, in agreement with experience. (The dihydrides apparently do not exist in the pure state although some trimethylamine complexes have been prepared [27].)

The equation for the disproportionation of Et_2AlH(T, l) is:

$$Et_2AlH(T, l) \rightarrow \tfrac{1}{3}AlH_3(c) + \tfrac{2}{3}Et_3Al(D, l)$$

$$\Delta H = +0.7$$

Since ΔS for the reaction is negative, ΔF is positive. This indicates that Et_2AlH(T, l) is thermodynamically stable with respect to disproportionation, in agreement with experience.

Heats of formation of the alkylaluminum halides

Diethylaluminum chloride

The heat of the following reaction was measured:

$$\tfrac{2}{3}EtAl(l) + \tfrac{1}{3}AlCl_3(c) \rightarrow Et_2AlCl(l) \qquad (14)$$

$$[\Delta H(\approx 25°) = -5.32 \pm 0.10 \text{ kcal/gfw } Et_2AlCl]$$

Using —45.9 ± 2.2 for ΔH^0_f of Et_3Al(l) (Table 9) and —168.65 ± 0.20** for ΔH^0_f of $AlCl_3$(c), ΔH^0_f of Et_2AlCl(l) is calculated as —92.14 ± 1.5 kcal/gfw.

---

* For $\frac{2}{3}AlCl_3(M, g) + \frac{1}{3}R_3Al(M, g) \rightarrow RAlCl_2(M, g)$, $\Delta H^0_{\text{red.}}$ was estimated as —4.7 from data in this paper. Assuming $\Delta H^0_{\text{red.}}(H)/\Delta H^0_{\text{red.}}(Cl) = 0.31$ as in previous footnote, $\Delta H^0_{\text{red.}}(H)$ is calculated as —1.5 kcal.

** See first footnote p. 187.

Diethylaluminum bromide

The heat of the following reaction was measured:

$\frac{2}{3}Et_3Al(l) + \frac{1}{3}AlBr_3(c) \rightarrow Et_2AlBr(l)$ (15)

$[\Delta H(\approx 25°) = -7.28 \pm 0.14$ kcal/gfw $Et_2AlBr]$

Using -45.9 ± 2.2 for ΔH_f^0 of $Et_3Al(l)$ (Table 9) and -122.16 ± 0.30[*] for ΔH_f^0 of $AlBr_3(c)$, ΔH_f^0 of $Et_2AlBr(l)$ is calculated as $-78.6_0 \pm 1.5$ kcal/gfw.

Diethylaluminum iodide

The heat of the following reaction was measured:

$\frac{2}{3}Et_3Al(l) + \frac{1}{3}AlI_3(c) \rightarrow Et_2AlI(l)$ (16)

$[\Delta H(\approx 25°) = -5.84 \pm 0.11$ kcal/gfw $Et_2AlI]$

Using -45.9 ± 2.2 for ΔH_f^0 of $Et_3Al(l)$ (Table 9) and -73.9 ± 1.5[*] for ΔH_f^0 of $AlI_3(c)$, ΔH_f^0 of $Et_2AlI(l)$ is calculated as $-61.0_7 \pm 1.6$ kcal/gfw.

Dialkylaluminum halides

The heats of formation of the liquid dialkylaluminum halides, $R_2AlX(l)$, were estimated from the corresponding values for the ethyl compounds as follows. Consider the redistribution reaction:

$\frac{2}{3}R_3Al(M, l) + \frac{1}{3}AlX_3(c) \rightarrow R_2AlX(D, l)$ (17)

$[\Delta H = \Delta H^0_{red.}(X)]$

For a particular X (Cl, Br or I), it is assumed that, to a good degree of approximation, $\Delta H^0_{red.}(X)$ has the same value for other R groups as for R = Et. This is equivalent to two other assumptions, the first of which is that ΔH for the reaction $\frac{2}{3}R_3Al(M, l) + \frac{1}{3}AlX_3(M, l) \rightarrow R_2AlX(M, l)$ does not vary significantly with the R-group[**]. This assumption is supported by direct measurements of heats of redistribution of metal alkyl—metal halide systems. Thus the results of the liquid-phase studies of Nash, Skinner and Stack [33] on the systems R_4Sn—$SnCl_4$ indicate that $\Delta H^0_{red.}$ does not vary appreciably when R is changed from Me to Et or Bu. (For the reaction $R_4Sn(l) + SnCl_4(l) \rightarrow R_3SnCl(l) + RSnCl_3(l)$, they reported $\Delta H = -22.1 \pm 2.2$ for R = Me, -22.6 ± 1.1 for R = Et and -22.1 ± 0.3 kcal for R = Bu.) In addition, the results of redistribution studies on the systems R_2Hg—HgX_2, summarized by Pritchard [34], indicate that for X = Cl, Br or I, $\Delta H^0_{red.}(g)$[***] does not vary significantly when R is changed from Me to Et or Pr. (The heats of redistribution in solution were measured directly [35] and converted into $\Delta H^0_{red.}$ for the gaseous reactions.) The second assumption is that ΔH of dissociation of $R_2AlX(D, l)$ to $R_2AlX(M, l)$

---

[*] Values were taken from the latest JANAF Tables [32]: 6—30—70 for $AlCl_3$, 6—30—72 for $AlBr_3$ and 6—30—64 for AlI_3.

[**] R is restricted to primary alkyl groups not associated with large steric effects.

[***] This same statement applies to $\Delta H^0_{red.}(l)$ since the value of the gas-to-liquid correction term does not vary significantly with the R-group. For a typical system [33], the difference in correction terms for Me and Et is <0.6 kcal/gfw of product. For Et and a larger group, the difference would be even smaller.

does not vary significantly with the R-group. This is surely reasonable since these dimers are well known to be halogen-bridged so that the nature of the R-group should have little effect on the heat of dissociation (again, bulky R-groups with large steric effects are excluded). The overall uncertainty of the combined assumptions is estimated as ±1.5 kcal/gfw R_2AlX.

The equations for the heats of formation of the dialkylaluminum halides are derived as follows, with reference to eqn. 17.

$$\begin{aligned}\Delta H^0_{\text{red.}}(\text{Cl}) &= \Delta H^0_f[\text{Et}_2\text{AlCl(l)}] - \tfrac{2}{3}\Delta H^0_f[\text{Et}_3\text{Al(M, l)}] - \tfrac{1}{3}\Delta H^0_f[\text{AlCl}_3\text{(c)}]\\ &= -92.1_4 - \tfrac{2}{3}(-37.4) - \tfrac{1}{3}(-168.65)\\ &= -10.9_9\end{aligned}$$

$$\begin{aligned}\Delta H^0_f[\text{R}_2\text{AlCl(l)}] &= \tfrac{2}{3}\Delta H^0_f[\text{R}_3\text{Al(M, l)}] + \tfrac{1}{3}\Delta H^0_f[\text{AlCl}_3\text{(c)}] + \Delta H^0_{\text{red.}}(\text{Cl})\\ &= \tfrac{2}{3}\Delta H^0_f[\text{R}_3\text{Al(M, l)}] + \tfrac{1}{3}(-168.65) - 10.9_9\end{aligned}$$

$$\Delta H^0_f[\text{R}_2\text{AlCl(l)}] = \tfrac{2}{3}\Delta H^0_f[\text{R}_3\text{Al(M, l)}] - 67.2_1$$

$$\begin{aligned}\Delta H^0_{\text{red.}}(\text{Br}) &= \Delta H^0_f[\text{Et}_2\text{AlBr(l)}] - \tfrac{2}{3}\Delta H^0_f[\text{Et}_3\text{Al(M, l)}] - \tfrac{1}{3}\Delta H^0_f[\text{AlBr}_3\text{(c)}]\\ &= -78.6_0 - \tfrac{2}{3}(-37.4) - \tfrac{1}{3}(-122.16)\\ &= -12.9_5\end{aligned}$$

$$\begin{aligned}\Delta H^0_f[\text{R}_2\text{AlBr(l)}] &= \tfrac{2}{3}\Delta H^0_f[\text{R}_3\text{Al(M, l)}] + \tfrac{1}{3}\Delta H^0_f[\text{AlBr}_3\text{(c)}] + \Delta H^0_{\text{red.}}(\text{Br})\\ &= \tfrac{2}{3}\Delta H^0_f[\text{R}_3\text{Al(M, l)}] + \tfrac{1}{3}(-122.16) - 12.9_5\end{aligned}$$

$$\Delta H^0_f[\text{R}_2\text{AlBr(l)}] = \tfrac{2}{3}\Delta H^0_f[\text{R}_3\text{Al(M, l)}] - 53.6_7 \tag{19}$$

$$\begin{aligned}\Delta H^0_{\text{red.}}(\text{I}) &= \Delta H^0_f[\text{Et}_2\text{AlI(l)}] - \tfrac{2}{3}\Delta H^0_f[\text{Et}_3\text{Al(M, l)}] - \tfrac{1}{3}\Delta H^0_f[\text{AlI}_3\text{(c)}]\\ &= -61.0_7 - \tfrac{2}{3}(-37.4) - \tfrac{1}{3}(-73.9)\\ &= -11.5_0\end{aligned}$$

$$\begin{aligned}\Delta H^0_f[\text{R}_2\text{AlI(l)}] &= \tfrac{2}{3}\Delta H^0_f[\text{R}_3\text{Al(M, l)}] + \tfrac{1}{3}\Delta H^0_f[\text{AlI}_3\text{(c)}] + \Delta H^0_{\text{red.}}(\text{I})\\ &= \tfrac{2}{3}\Delta H^0_f[\text{R}_3\text{Al(M, l)}] + \tfrac{1}{3}(-73.9) - 11.5_0\end{aligned}$$

$$\Delta H^0_f[\text{R}_2\text{AlI(l)}] = \tfrac{2}{3}\Delta H^0_f[\text{R}_3\text{Al(M, l)}] - 36.1_3 \tag{20}$$

Values of ΔH^0_f(l) for the dialkylaluminum chlorides calculated from eqn. 18 are listed in column 3 of Table 14 where they are compared with observed values. Agreement is satisfactory only in the case of i-Bu_2AlCl. The seven values reported by Pawlenko [1], based on heat of combustion measurements, are not self-consistent thermodynamically. The increments from Et_2AlCl to Pr_2AlCl (≈43 kcal) and from Pr_2AlCl to Bu_2AlCl (≈28 kcal) are far too large. The apparent decrease in $-\Delta H^0_f$(l) from Bu_2AlCl to Hx_2AlCl to Oc_2AlCl* cannot possibly be correct.

Calculated values for the heat of reaction of R_3Al(l) with $AlCl_3$(c) to form R_2AlCl(D, l) are given in Table 15. The ΔH values based on the calculated ΔH^0_f

---

* Hx = hexyl; Oc = octyl.

TABLE 14

HEATS OF FORMATION OF DIALKYLALUMINUM CHLORIDES

Compound[a]	$-\Delta H_f^0$(calculated)		$-\Delta H_f^0$(D, l) (exptl.)	
	(D, g)[b]	(D, l)[c]	Pawlenko[d]	Shaulov[e]
Me_2AlCl	79.9	84.7		
Et_2AlCl	85.0	92.1	56.9	99.2
Pr_2AlCl	95.1	104.1	99.8	
Bu_2AlCl	105.1	116.1	127.4	
Pe_2AlCl	115.2	128.1		
Hx_2AlCl	125.2	140.1	73.1	
Hp_2AlCl	135.3	152.1		
Oc_2AlCl	145.3	164.1	18.8	
[Increment]	[10.0$_5$]	[12.0]		
i-Bu_2AlCl	109.0	119.5	118.7	117.4
i-Pe_2AlCl	118.7	131.2		
i-Hx_2AlCl	128.3	142.8	92.2	
i-Hp_2AlCl	138.3	154.8		
i-Oc_2AlCl	148.3	166.8		
[Increment]	[10.0]	[12.0]		

[a] For the iso-compounds with R ≠ i-Bu, as in previous and succeeding tables, the point of attachment of the R group to the Al atom is remote from the branched end of the group. [b] Calculated from corresponding value for (D, l) by subtracting the heat of vaporization (the ΔH_v^0(D) value for Et_2AlCl is from ref. 37; other values were estimated). Estimated uncertainties: ±1.5 for Et_2AlCl; from ±2.1 for Me_2AlCl to ±2.3 for Oc_2AlCl. [c] Value listed for Et_2AlCl is experimental. Other values were calculated from eqn. 18. Estimated uncertainties: ±1.5 for Et_2AlCl; ±2.1 for all other compounds. [d] Ref. 1. [e] Ref. 36.

values range from —4.5 to —10.3. This indicates that the reaction is moderately exothermic, in agreement with experience (the value of —5.3 for R = Et is experimental). The two values based on Shaulov's [36] measurements agree fairly

TABLE 15

ΔH OF REACTION: $\frac{2}{3}R_3Al(l) + \frac{1}{3}AlCl_3(c) \rightarrow R_2AlCl(D, l)$

R	ΔH of reaction based on ΔH_f^0 values from:		
	This paper	Pawlenko[a]	Shaulov[b]
Me	— 4.5		
Et	— 5.3[c]	37.1	— 8.4
Pr	— 5.8	7.8	
Bu	— 6.0	— 11.8	
Pe	— 6.1		
Hx	— 6.1	60.9[d]	
Hp	— 6.1		
Oc	— 6.1	139.2[d]	
i-Bu	—10.3	— 0.6	—14.6
i-Pe	— 6.3		
i-Hx	— 6.1	44.5[d]	
i-Hp	— 6.1		
i-Oc	— 6.1		

[a] Ref. 1. [b] Ref. 36. [c] Direct experimental value. [d] Value of $\Delta H_f^0[R_3Al(l)]$ was taken from this paper since it was not given by Pawlenko.

well with corresponding values based on the calculated ΔH_f^0 values. Of the seven values based on Pawlenko's measurements, only one (R = Bu) is in reasonable agreement with experience. The four large positive values are completely inconsistent with experience since they indicate that no reaction should occur (the corresponding ΔF values are also large and positive). It is therefore recommended that the calculated values of $\Delta H_f^0(l)$ for the dialkylaluminum chlorides be used in preference to the experimental values.

Values of $\Delta H_f^0(l)$ for the dialkylaluminum bromides and iodides, calculated from eqns. 19 and 20, are tabulated in Table 16 along with corresponding values of $\Delta H_f^0(D, g)$. There are no experimental values available for comparison.

Ethylaluminum dichloride

The heat of the following reaction was measured:

$$Et_3Al(l) + EtAlCl_2(l) \rightarrow 2\ Et_2AlCl(l)$$

$$[\Delta H(\approx 25°) = -9.44 \pm 0.18 \text{ kcal/gfw } EtAlCl_2]$$

On multiplying equation 14 by two and substracting the above equation from it, the following equation is obtained:

$$\tfrac{1}{3}Et_3Al(l) + \tfrac{2}{3}AlCl_3(c) \rightarrow EtAlCl_2(l)$$

$$[\Delta H(\approx 25°C) = -1.20 \pm 0.27 \text{ kcal/gfw } EtAlCl_2]$$

Using -45.9 ± 2.2 for ΔH_f^0 of $Et_3Al(l)$ (Table 9) and -168.65 ± 0.20 [32] for ΔH_f^0 of $AlCl_3(c)$, ΔH_f^0 of $EtAlCl_2(l)$ is calculated as $-128.9_3 \pm 0.8$ kcal/gfw.

TABLE 16

HEATS OF FORMATION OF DIALKYLALUMINUM BROMIDES AND IODIDES

Compound	$-\Delta H_f^0$ for X=Br		$-\Delta H_f^0$ for X = I	
	(D, g)[a]	(D, l)[b]	(D, g)[a]	(D, l)[c]
Me_2AlX	65.8	71.2	47.2	53.7
Et_2AlX	70.9	78.6	52.3	61.1
Pr_2AlX	81.0	90.6	62.4	73.1
Bu_2AlX	91.0	102.6	72.4	85.1
Pe_2AlX	101.1	114.6	82.5	97.1
Hx_2AlX	111.1	126.6	92.5	109.1
Hp_2AlX	121.2	138.6	102.6	121.1
Oc_2AlX	131.2	150.6	112.6	133.1
[Increment]	[10.0_5]	[12.0]	[10.0_5]	[12.0]
i-Bu_2AlX	94.8	105.9	76.2	88.4
i-Pe_2AlX	104.6	117.7	85.9	100.1
i-Hx_2AlX	114.2	129.3	95.5	111.7
i-Hp_2AlX	124.2	141.3	105.5	123.7
i-Oc_2AlX	134.2	153.3	115.5	135.7
[Increment]	[10.0]	[12.0]	[10.0]	[12.0]

[a] Calculated from corresponding value for (D, l) by subtracting the heat of vaporization (the $\Delta H_v^0(D)$ value for Et_2AlI is from ref. 37; other values were estimated). Estd. uncertainties: ±1.5 for Et_2AlBr; from ±2.1 for Me_2AlBr to ±2.3 for Oc_2AlBr; ±1.7 for Et_2AlI; from ±2.2 for Me_2AlI to ±2.4 for Oc_2AlI.

[b] Value for Et_2AlBr is experimental. Other values were calculated from eqn. 19. Estimated uncertainties: ± 1.5 for Et_2Albr; ± 2.1 for all other bromides.

[c] Value for Et_2AlI is experimental. Other values were calculated from eqn. 20. Estimated uncertainties: ±1.6 for Et_2AlI; ±2.2 for all other iodides.

Ethylaluminum dibromide

The heat of the following reaction was measured:

$Et_3Al(l) + EtAlBr_2(l) \rightarrow 2\ Et_2AlBr(l)$

$[\Delta H(\approx 25°) = -9.49 \pm 0.18$ kcal/gfw $EtAlBr_2]$

On doubling equation 15 and subtracting the above equation from it, the following equation is obtained:

$\frac{1}{3}Et_3Al(l) + \frac{2}{3}AlBr_3(c) \rightarrow EtAlBr_2(l)$

$[\Delta H(\approx 25°C) = -5.07 \pm 0.33$ kcal/gfw $EtAlBr_2]$

Using -45.9 ± 2.2 for ΔH_f^0 of $Et_3Al(l)$ (Table 9) and -122.16 ± 0.30 [32] for ΔH_f^0 of $AlBr_3(c)$, ΔH_f^0 of $EtAlBr_2$ (l) is calculated as $-101.8_1 \pm 0.8$ kcal/gfw.

Ethylaluminum diiodide

The heat of the following reaction was measured:

$Et_3Al(l) + EtAlI_2(l) \rightarrow 2\ Et_2AlI(l)$

$[\Delta H(\approx 25°) = -8.65 \pm 0.17$ kcal/gfw $EtAlI_2]$

On doubling eqn. 16 and substracting the above equation from it, the following equation is obtained:

$\frac{1}{3}Et_3Al(l) + \frac{2}{3}AlI_3(c) \rightarrow EtAlI_2(l)$

$[\Delta H(\approx 25°) = -3.03 \pm 0.28$ kcal/gfw $EtAlI_2]$

Using -45.9 ± 2.2 for ΔH_f^0 of $Et_3Al(l)$ (Table 9) and -73.9 ± 1.5 [32] for ΔH_f^0 of $AlI_3(c)$, ΔH_f^0 of $EtAlI_2$ (l) is calculated as $-67.6_0 \pm 1.3$ kcal/gfw.

Alkylaluminum dihalides

The heats of formation of the liquid alkylaluminum dihalides, $RAlX_2(l)$, were estimated from the corresponding values for the ethyl compounds as follows. Consider the redistribution reaction:

$$\frac{1}{3}R_3Al(M, l) + \frac{2}{3}AlX_3(c) \rightarrow RAlX_2(D, l)$$
$$[\Delta H = \Delta H^0_{red.}(X)] \tag{21}$$

For a particular X (Cl, Br or I), it is assumed that $\Delta H^0_{red.}(X)$ has the same value (within the estimated uncertainty of ±1.5 kcal) for other R groups as for R = Et. The basis for this assumption is the same as that given for the dialkylaluminum halides. With reference to eqn. 21, the heats of formation of the alkylaluminum dihalides are derived as follows:

$$\begin{aligned}\Delta H^0_{red.}(Cl) &= \Delta H_f^0[EtAlCl_2(l)] - \tfrac{1}{3}\Delta H_f^0[Et_3Al(M, l)] - \tfrac{2}{3}\Delta H_f^0[AlCl_3(c)]\\ &= -128.9_3 - \tfrac{1}{3}(-37.4) - \tfrac{2}{3}(-168.65)\\ &= -4.0_3\end{aligned}$$

$$\begin{aligned}\Delta H_f^0[RAlCl_2(l)] &= \tfrac{1}{3}\Delta H_f^0[R_3Al(M, l)] + \tfrac{2}{3}\Delta H_f^0[AlCl_3(c)] + \Delta H^0_{red.}(Cl)\\ &= \tfrac{1}{3}\Delta H_f^0[R_3Al(M, l)] + \tfrac{2}{3}(-168.65) - 4.0_3\end{aligned}$$

$$\Delta H_f^0[\mathrm{RAlCl_2(l)}] = \tfrac{1}{3}\Delta H_f^0[\mathrm{R_3Al(M, l)}] - 116.4_6 \tag{22}$$

$$\begin{aligned}\Delta H^0_{\text{red.}}(\mathrm{Br}) &= \Delta H_f^0[\mathrm{EtAlBr_2(l)}] - \tfrac{1}{3}\Delta H_f^0[\mathrm{Et_3Al(M, l)}] - \tfrac{2}{3}\Delta H_f^0[\mathrm{AlBr_3(c)}]\\ &= -101.8_1 - \tfrac{1}{3}(-37.4) - \tfrac{2}{3}(-122.16)\\ &= -7.9_0\end{aligned}$$

$$\begin{aligned}\Delta H_f^0[\mathrm{RAlBr_2(l)}] &= \tfrac{1}{3}\Delta H_f^0[\mathrm{R_3Al(M, l)}] + \tfrac{2}{3}\Delta H_f^0[\mathrm{AlBr_3(c)}] + \Delta H^0_{\text{red.}}(\mathrm{Br})\\ &= \tfrac{1}{3}\Delta H_f^0[\mathrm{R_3Al(M, l)}] + \tfrac{2}{3}(-122.16) - 7.9_0\end{aligned}$$

$$\Delta H_f^0[\mathrm{RAlBr_2(l)}] = \tfrac{1}{3}\Delta H_f^0[\mathrm{R_3Al(M, l)}] - 89.3_4 \tag{23}$$

$$\begin{aligned}\Delta H^0_{\text{red.}}(\mathrm{I}) &= \Delta H_f^0[\mathrm{EtAlI_2(l)}] - \tfrac{1}{3}\Delta H_f^0[\mathrm{Et_3Al(M, l)}] - \tfrac{2}{3}\Delta H_f^0[\mathrm{AlI_3(c)}]\\ &= -67.6_0 - \tfrac{1}{3}(-37.4) - \tfrac{2}{3}(-73.9)\\ &= -5.8_7\end{aligned}$$

$$\begin{aligned}\Delta H_f^0[\mathrm{RAlI_2(l)}] &= \tfrac{1}{3}\Delta H_f^0[\mathrm{R_3Al(M, l)}] + \tfrac{2}{3}\Delta H_f^0[\mathrm{AlI_3(c)}] + \Delta H^0_{\text{red.}}(\mathrm{I})\\ &= \tfrac{1}{3}\Delta H_f^0[\mathrm{R_3Al(M, l)}] + \tfrac{2}{3}(-73.9) - 5.8_7\end{aligned}$$

$$\Delta H_f^0[\mathrm{RAlI_2(l)}] = \tfrac{1}{3}\Delta H_f^0[\mathrm{R_3Al(M, l)}] - 55.1_4 \tag{24}$$

Values of $\Delta H_f^0(\mathrm{l})$ for the alkylaluminum dichlorides calculated from eqn. 22 are tabulated in column 3 of Table 17 where they are compared with Pawlenko's [1] experimental values. Again, Pawlenko's results are not self-consistent ther-

TABLE 17

HEATS OF FORMATION OF ALKYLALUMINUM DICHLORIDES

Compound	$-\Delta H_f^0$(calculated)		$-\Delta H_f^0$(D, l) (exptl.) (Pawlenko)[c]
	(D, g)[a]	(D, l)[b]	
$\mathrm{MeAlCl_2}$	119.7	125.2	
$\mathrm{EtAlCl_2}$	122.2	128.9	75.4
$\mathrm{PrAlCl_2}$	127.1	134.9	118.9
$\mathrm{BuAlCl_2}$	132.0	140.9	73.2
$\mathrm{PeAlCl_2}$	136.9	146.9	
$\mathrm{HxAlCl_2}$	141.8	152.9	68.9
$\mathrm{HpAlCl_2}$	146.7	158.9	
$\mathrm{OcAlCl_2}$	151.6	164.9	9.6
[Increment]	[4.9]	[6.0]	
i-$\mathrm{BuAlCl_2}$	134.0	142.6	71.5
i-$\mathrm{PeAlCl_2}$	138.8	148.5	
i-$\mathrm{HxAlCl_2}$	143.4	154.3	89.8
i-$\mathrm{HpAlCl_2}$	148.3	160.3	
i-$\mathrm{OcAlCl_2}$	153.1	166.3	
[Increment]	[4.8_5]	[6.0]	

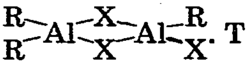
[a] Calculated from corresponding value for (D, l) by subtracting the heat of vaporization (ΔH_v^0(D) values for $\mathrm{EtAlCl_2}$ and i-$\mathrm{BuAlCl_2}$ are from ref. 37; other values were estimated). Estimated uncertainties: ±0.9 for $\mathrm{EtAlCl_2}$; from ±1.7 for $\mathrm{MeAlCl_2}$ to ±1.8 for $\mathrm{OcAlCl_2}$. [b] Value listed for $\mathrm{EtAlCl_2}$ is experimental. Other values were calculated from eqn. 22. Estimated uncertainties: ±0.8 for $\mathrm{EtAlCl_2}$; ±1.7 for all other compounds. [c] Ref. 1.

modynamically. The apparent decrease in $-\Delta H_f^0(l)$ from $PrAlCl_2$ to $BuAlCl_2$ to $HxAlCl_2$ and especially to $OcAlCl_2$ cannot be correct.

Calculated values of ΔH for the reaction of $R_3Al(l)$ with $AlCl_3(c)$ to form $RAlCl_2(D, l)$ are given in Table 18. The ΔH values based on the calculated ΔH_f^0 values indicate that the reaction is mildly exothermic, in agreement with experience (the value of —1.2 for R = Et, for example, was calculated from experimental data on two related reactions). The ΔH values based on Pawlenko's experimental ΔH_f^0 values are all large and positive, ranging from 19 to 154 kcal in a most erratic fashion. They are totally inconsistent with experience since they indicate that no reaction should occur (the corresponding ΔF values are also large and positive). It is therefore recommended that the calculated values of $\Delta H_f^0(l)$ for the alkylaluminum dichlorides be used in preference to Pawlenko's experimental values.

Values of $\Delta H_f^0(l)$ for the alkylaluminum dibromides and diiodides calculated from eqns. 23 and 24 are listed in Table 19 along with corresponding values of $\Delta H_f^0(D, g)$. There are no experimental values available for comparison.

Ethylaluminum sesquichloride

When a gfw of liquid R_2AlX is mixed with a gfw of liquid $RAlX_2$, the resulting equilibrium mixture is termed an alkylaluminum sesquihalide and its formula is customarily written as $R_3Al_2X_3$. The reaction is mildly exothermic corresponding to partial conversion (statistically, 50%) to the mixed dimer . The heat of the following reaction was measured:

$$Et_2AlCl(l) + EtAlCl_2(l) \rightarrow Et_3Al_2Cl_3(l)$$

$$[\Delta H(\approx 25°) = \Delta H_r^0(Cl) = -0.54^* \pm 0.05 \text{ kcal/gfw } Et_3Al_2Cl_3]$$

TABLE 18

ΔH OF REACTION: $\frac{1}{3}R_3Al(l) + \frac{2}{3}AlCl_3(c) \rightarrow RAlCl_2(D, l)$

R	ΔH_r based of ΔH_f^0 values from:	
	This paper	Pawlenko[a]
Me	—0.8	
Et	—1.2	55.9
Pr	—1.4	19.2
Bu	—1.5	68.9
Pe	—1.6	
Hx	—1.6	82.4[b]
Hp	—1.6	
Oc	—1.6	153.7[b]
i-Bu	—3.7	71.9
i-Pe	—1.7	
i-Hx	—1.6	62.9[b]
i-Hp	—1.6	
i-Oc	—1.7	

[a] Ref. 1. [b] Value of $\Delta H_f^0[R_3Al(l)]$ was taken from this paper since it was not given by Pawlenko.

---

[*] This is appreciably lower in magnitude than the values ($-\Delta H_r^0 \geq 1.0$ kcal) reported by Brandt and Hoffmann [38] for $Me_3Al_2Cl_3$ and $Et_3Al_2Cl_3$.

TABLE 19

HEATS OF FORMATION OF ALKYLALUMINUM DIBROMIDES AND DIIODIDES

Compound	$-\Delta H_f^0$ for X=Br		$-\Delta H_f^0$ for X=I	
	(D, g)[a]	(D, l)[b]	(D, g)[a]	(D, l)[c]
$MeAlX_2$	90.9	98.1	53.7	63.9
$EtAlX_2$	93.4	101.8	56.2	67.6
$PrAlX_2$	98.3	107.8	61.1	73.6
$BuAlX_2$	103.2	113.8	66.0	79.6
$PeAlX_2$	108.1	119.8	70.9	85.6
$HxAlX_2$	113.0	125.8	75.8	91.6
$HpAlX_2$	117.9	131.8	80.7	97.6
$OcAlX_2$	122.8	137.8	85.6	103.6
[Increment]	[4.9]	[6.0]	[4.9]	[6.0]
i-$BuAlX_2$	105.2	115.5	68.0	81.3
i-$PeAlX_2$	109.9	121.3	72.7	87.1
i-$HxAlX_2$	114.5	127.1	77.3	92.9
i-$HpAlX_2$	119.4	133.1	82.2	98.9
i-$OcAlX_2$	124.2	139.1	87.0	104.9
[Increment]	[4.8_5]	[6.0]	[4.8_5]	[6.0]

[a] Calculated from corresponding value for (D, l) by subtracting the heat of vaporization (ΔH_v^0(D) values for $EtAlBr_2$ and $EtAlI_2$ are from ref. 37; other values were estimated). Estimated uncertainties: ±0.9 for Et_2AlBr_2; from ± 1.7 for $MeAlBr_2$ to ± 1.9 for $OcAlBr_2$; ± 1.4 for $EtAlI_2$; from ± 2.1 for $MeAlI_2$ to ± 2.2 for $OcAlI_2$.

[b] Value for $EtAlBr_2$ is experimental. Other values were calculated from eqn. 23. Estimated uncertainties: ±0.8 for $EtAlBr_2$; ±1.7 for all other bromides. [c] Value for $EtAlI_2$ is experimental. Other values were calculated from eqn. 24. Estimated uncertainties: ±1.3 for $EtAlI_2$; ±2.0 for all other iodides.

Using ΔH_f^0 values derived herein for $Et_2AlCl(l)$ and $EtAlCl_2(l)$, ΔH_f^0 of $Et_3Al_2Cl_3(l)$ is calculated as $-92.1_4-128.9_3-0.54=-221.6_1 \pm 1.7$ kcal/gfw.

Ethylaluminum sesquibromide

The heat of the following reaction was measured:

$$Et_2AlBr(l) + EtAlBr_2(l) \rightarrow Et_3Al_2Br_3(l)$$

$$[\Delta H(\approx 25°) = \Delta H_r^0(Br) = -0.59 \pm 0.05 \text{ kcal/gfw } Et_3Al_2Br_3]$$

Using ΔH_f^0 values derived herein, ΔH_f^0 of $Et_3Al_2Br_3(l)$ is calculated as $-78.6_0 - 101.8_1 - 0.59 = -181.0_0 \pm 1.7$ kcal/gfw.

Alkylaluminum sesquihalides

Equations for the heats of formation of the liquid alkylaluminum sesquihalides, $R_3Al_2X_3$, were obtained by summing the corresponding equations for $R_2AlX(l)$ and $RAlX_2(l)$ and adding corresponding values of $\Delta H_r^0(X)$. For the chlorides and bromides, the values determined experimentally for R = Et were assumed to apply to other R groups. For the iodides, the estimated value $\Delta H_r^0(I) = -0.5$ kcal/gfw $R_3Al_2I_3$ was used. The following equations were derived in this manner:

$$\Delta H_f^0[R_3Al_2Cl_3(l)] = \Delta H_f^0[R_3Al(M, l)] - 184.2_1 \quad (25)$$

$$\Delta H_f^0[R_3Al_2Br_3(l)] = \Delta H_f^0[R_3Al(M, l)] - 143.6_0 \quad (26)$$

$$\Delta H_f^0[R_3Al_2I_3(l)] = \Delta H_f^0[R_3Al(M, l)] - 91.7_7 \quad (27)$$

TABLE 20

HEATS OF FORMATION OF ALKYLALUMINUM SESQUIHALIDES

Compound	$-\Delta H_f^0$(l) for X=Cl		$-\Delta H_f^0$(l) (calcd.) for:	
	Calcd.[a]	Pawlenko[b]	X=Br[c]	X=I[d]
$Me_3Al_2X_3$	210.5		169.9	118.1
$Et_3Al_2X_3$	221.6	139.6	181.0	129.2
$Pr_3Al_2X_3$	239.6	226.1	199.0	147.2
$Bu_3Al_2X_3$	257.6	186.7	217.0	165.2
$Pe_3Al_2X_3$	275.6		235.0	183.2
$Hx_3Al_2X_3$	293.6	126.9	253.0	201.2
$Hp_3Al_2X_3$	311.6		271.0	219.2
$Oc_3Al_2X_3$	329.6	24.3	289.0	237.2
[Increment]	[18.0]		[18.0]	[18.0]
i-$Bu_3Al_2X_3$	262.6	195.3	222.0	170.2
i-$Pe_3Al_2X_3$	280.2		239.6	187.8
i-$Hx_3Al_2X_3$	297.6	183.0	257.0	205.2
i-$Hp_3Al_2X_3$	315.6		275.0	223.2
i-$Oc_3Al_2X_3$	333.6		293.0	241.2
[Increment]	[18.0]		[18.0]	[18.0]

[a] Value for $Et_3Al_2Cl_3$ is experimental. Other values were calculated from eqn. 25. Estd. uncert.: ±1.7 for $Et_3Al_2Cl_3$; ±2.7 for all other chlorides. [b] Ref. 1. [c] Value for $Et_3Al_2Br_3$ is experimental. Other values were calculated from eqn. 26. Estd. uncert.: ±1.7 for $Et_3Al_2Br_3$; ±2.7 for all other bromides. [d] Calculated from eqn. 27. Estd. uncert.: ±2.1 for $Et_3Al_2I_3$; ±3.0 for all other iodides.

Calculated ΔH_f^0(l) values for the sesquihalides (eqns. 25—27) are listed in Table 20. The values for the sesquichlorides are compared with Pawlenko's [1] experimental values. Except for $Pr_3Al_2Cl_3$, the experimental $-\Delta H_f^0$ values are much smaller than the corresponding calculated values. Again, Pawlenko's results are not self-consistent thermodynamically. The apparent stepwise decrease in $-\Delta H_f^0$(l) from R = Pr to R = Oc cannot possibly be correct.

TABLE 21

ΔH OF REACTION: $R_3Al(l) + AlCl_3(c) \rightarrow R_3Al_2Cl_3(l)$

R	ΔH_r based on ΔH_f^0 values from:	
	This paper	Pawlenko[a]
Me	− 5.9	
Et	− 7.1	85.7
Pr	− 7.9	19.6
Bu	− 8.2	71.0
Pe	− 8.2	
Hx	− 8.3	158.5[b]
Hp	− 8.3	
Oc	− 8.4	297.0[b]
i-Bu	−14.5	66.2
i-Pe	− 8.6	
i-Hx	− 8.3	106.4[b]
i-Hp	− 8.3	
i-Oc	− 8.4	

[a] Ref. 1. [b] Value of $\Delta H_f^0[R_3Al(l)]$ was taken from this paper since it was not given by Pawlenko.

TABLE 22

ΔH OF REACTION: $3\ RX(l\ or\ g) + 2\ Al(c) \rightarrow R_3Al_2X_3(l)$

$R_3Al_2X_3$	$-\Delta H_r^a$ for:	
	RX(l)	RX(g)
$Me_3Al_2Cl_3$		148.6
$Et_3Al_2Cl_3$	124.1	141.5[b]
$Pr_3Al_2Cl_3$	125.6	146.3
$Me_3Al_2Br_3$		142.9
$Et_3Al_2Br_3$	115.3	135.1
$Pr_3Al_2Br_3$	112.6	136.0
$Me_3Al_2I_3$	108.2	128.1
$Et_3Al_2I_3$	100.1	123.2
$Pr_3Al_2I_3$	99.5	125.3

[a] Using calculated $\Delta H_f^0(l)$ values for $R_3Al_2X_3$; $\Delta H_f^0[RX]$ values from ref. 40. [b] Pawlenko [1] reported 17.5 which is cited by Mole and Jeffery [39], page 12.

Calculated values of ΔH for the reaction of $R_3Al(l)$ with $AlCl_3(c)$ to form $R_3Al_2Cl_3(l)$ are listed in Table 21. The ΔH values based on the calculated ΔH_f^0 values indicate that the reaction is moderately exothermic, in agreement with experience. The ΔH values based on Pawlenko's measured ΔH_f^0 values are all large and positive. They are inconsistent with experience since they indicate that the reaction is highly endothermic and should not occur (the corresponding ΔF values are also large and positive). It is therefore recommended that the calculated values of $\Delta H_f^0(l)$ for the alkylaluminum sesquichlorides be used in preference to Pawlenko's experimental values.

An important method for the laboratory preparation of alkylaluminum compounds consists of the reaction of an alkyl halide with aluminum to form the corresponding alkylaluminum sesquihalide: $3RX(l\ or\ g) + 2Al(c) \rightarrow R_3Al_2X_3(l)$. The reaction has been described [27] as "strongly exothermic." Calculated values of ΔH_r (Table 22) indicate that the reaction is indeed strongly exothermic. For EtCl(g), for example, $-\Delta H_r = 141.5$ kcal/gfw of $Et_3Al_2Cl_3$. This is much larger than the value (17.5) given by Pawlenko [1] and cited by Mole and Jeffery [39] in their recent book (page 12). When one considers that the reaction involves the formation of three primary Al—Cl bonds and three primary Al—C bonds (at the mere expense of breaking three relatively weak C—Cl bonds), it becomes obvious that $-\Delta H_r$ must be far greater than 17.5 kcal. The calculated values are therefore more realistic and their use is recommended.

Conclusions

In conclusion, the heats of formation of aluminum alkyls and related compounds tabulated in this paper are believed to represent fairly the experimental ΔH_f^0 values thus far determined. When better experimental values become available, the methods here employed can be used in revising the tables. Definitive ΔH_f^0 values for $Me_3Al(l)$ and $Et_3Al(l)$ would provide a test of the "Extended Displacement Rule for Metals," which is of both theoretical and practical interest. These values could be used to calculate reasonably accurate ΔH_f^0 values for all the aluminum primary alkyls. The latter, in turn, could be combined with the experimental heat of redistribution data to produce revised tables for the alkylaluminum halides. Definitive ΔH_f^0 values for one or two hydrides (for example, Et_2AlH and i-Bu_2AlH) would lead to better ΔH_f^0 values for all the hydrides.

Experimental heats of formation of aluminum alkyls and related aluminum compounds thus far determined by combustion calorimetry have been shown to be thermodynamically inconsistent and unreliable. A far better approach for these compounds, and for organometallic compounds in general, is by reaction calorimetry in a rotating bomb. Such reactions are much less exothermic than combustion and if the reactions are well chosen, their heats can be measured with much smaller absolute error. Measurement of the heat of acid hydrolysis appears to be particularly appropriate for aluminum compounds (the heat of formation of $AlCl_3$ in aqueous HCl of various strengths has been reported [28, 41]. Measurements made thus far by this method [21, 36] indicate that the method shows promise, although the results obtained are not definitive.

Heats of vaporization

Where Antoine constants were available, ΔH_{vb} was first calculated via the Clapeyron equation. $\Delta H_v^0(25°)$ was then estimated using the "Watson Correlation" as described earlier [14]. Where boiling points were known, but not Antoine constants (usually the case for R = Me, Et), values of ΔS_{vb} were read from plots (ΔS_{vb} vs. t_b) developed for hydrocarbon analogs. After calculation of ΔH_{vb} from ΔS_{vb}, $\Delta H_v^0(25°)$ was estimated as above. Where boiling points were not known (usually the case for R = Pr and higher), increments in ΔH_v^0 (25°) corresponding to unit increases in the length of the R group were estimated as being equal to corresponding increments for the hydrocarbon analogs [6, 40, 42]. Since $\Delta H_v^0(25°)$ values for branched hydrocarbons are not available for carbon numbers above 10, these values were usually estimated via the Greenshields—Rossini equation [43]*:

$$\Delta H_v^0(25°, \text{isomer}) - \Delta H_v^0(25°, \text{normal}) = -0.118\, C_3 - 0.307\, C_4$$

---

* Due to a typographical error, the minus sign preceding the first term was omitted in the original paper (ref. 43, eqn. 6). The first term, like the second, should carry a minus sign since it contributes toward increased molecular compactness of the branched compound (with respect to the normal compound) and therefore contributes toward reduced ΔH_v^0. (Note, e.g. that the sign of the first term is the same as that of the second term in each of related eqns. 1 to 5 of ref. 43. Note also that the minus sign must be used with the first term of eqn. 6 in order to obtain ΔH_v^0 (isomer) — ΔH_v^0 (normal) = —1.34 as given by the authors in the example on page 274 of the paper.) Unfortunately this sign omission has been duplicated elsewhere and has led to incorrect results in the application of the equation. For example, the equation is given incorrectly in the recent book by Cox and Pilcher (ref. 2, p. 121). Thus the value calculated for ΔH_v^0(isopentane) — ΔH_v^0(n-pentane) on p. 122 of the book should be —0.43 kcal (rather than —0.19) which agrees much more closely with the experimental value (—0.42). A second example is found in a recent paper by E. Morawetz [44] in which erroneous ΔH_v^0 values for 28 compounds were calculated via eqn. 28. (Errors in the signs of the contributions were also made here in connection with the fourth or P_3 term. These errors affected the ΔH_v^0 values for 20 of the compounds.)

$$-\frac{3.081(Wn-Wi)}{N(N-1)}+0.164(P_{3i}-P_{3n})\text{kcal} \qquad (28)$$

In this equation, C_3 and C_4 are the numbers of tertiary and quaternary carbon atoms in the branched compound; P_3 is the total number of pairs of C atoms three bonds apart (i = isomer, n = normal); W, the Wiener number, is the total number of bonds between all pairs of C atoms and N is the number of C atoms. Increments were calculated in this fashion for both the n-R compounds and the i-R compounds, as well as differences between the n-butyl and the corresponding i-butyl compounds. It was found that within each series of n-R compounds, a constant increment in $\Delta H_v^0(25°)$ was obtained. Within each series of i-R compounds, on the other hand, the increment showed a slight increase with increasing N, hence an average value was used.

For $Me_2AlH(M)$, $\Delta H_v^0(25°)$ was estimated from that of $Me_3Al(M)$ by subtracting from it the difference in the corresponding hydrocarbon analogs. For $Et_2AlH(M)$, $\Delta H_v^0(25°)$ was estimated in the same fashion from that of $Et_3Al(M)$, the value for the latter having been estimated from its boiling point [14]. The $\Delta H_v^0(25°)$ values for the higher homologs were estimated by the incremental method described above.

Experimental

Materials

Anhydrous aluminum halides were as follows: $AlCl_3(c)$ (Alfa Inorganics, 99.999%); $AlBr_3(c)$ and $AlI_3(c)$ (Research Organic/Inorganic Chemical Corp., 99.5%). The specified purities were checked by chemical analysis and the materials used without further purification. Hexadecane (Humphrey Chemical Co., 99+%) was deoxygenated by bubbling dry N_2 through it for several hours and was stored over molecular sieves. The following were supplied by Ethyl Corporation, the indicated purities being established by chemical analysis: $Et_3Al(l)$, 98.0%; $EtAlCl_2(c)$, 98.5%; $EtAlBr_2(l)$, 99.0%; $EtAlI_2(c)$, 98.5%; $Et_2AlCl(l)$, 98.0%; and $Et_2AlI(l)$, 99.0%. $Et_2AlBr(l)$ was prepared by mixing stoichiometric amounts of Et_3Al and pre-chilled $EtAlBr_2$. All materials were stored in a dry N_2 box and the containers opened inside the box. Aluminum halides were transferred to glass vials which were weighed accurately before and after the vials were emptied into the calorimeter (the latter was brought into the dry box for this transfer). Liquids were transferred with hypodermic syringes which were weighed accurately before and after they were emptied into the N_2-flushed calorimeter. $EtAlCl_2(c)$ and $EtAlI_2(c)$ were melted and then transferred in the same fashion.

Calorimeter

The calorimeter consisted of a 180 ml, 3.4 cm (inside diameter) clear borosilicate glass Dewar fitted with a rubber stopper. A precision-type thermometer (−1 to +51° with 0.1° subdivisions) was mounted tightly in the stopper. Temperatures were read to the nearest 0.01° with the aid of a reading lens clamped to the thermometer. A slight pressure of dry N_2 was applied to the inside of the calorimeter through a hypodermic needle which penetrated the stopper (pressure control was facilitated by using an oil-filled bubbler in parallel with the needle). A short glass tube mounted in the stopper served as an entry port for the introduction of liquids into the calorimeter (this tube was kept closed except during these transfers). Stirring was magnetic using a Teflon-covered bar. The heat capacity of the calorimeter was evaluated by bringing it to a steady temperature near ambient, rapidly introducing a measured quantity (≈ 40 ml) of n-hexadecane at a known temperature several degrees above ambient, and measuring the equilibrium temperature. A plot was made of calorimeter heat capacity vs. liquid volume.

Thermochemical measurements

In a typical experiment of the type $2/3\ Et_3Al(l) + 1/3\ AlX_3(c) \rightarrow Et_2AlX(l)$, ≈ 0.01 gfw of finely divided $AlX_3(c)$ (crushed, if necessary) was weighed into the calorimeter and covered with a weighed amount (≈ 40 ml) of hexadecane (the latter, which is inert toward these chemicals, served to moderate the reaction and to limit the temperature rise). A suitable amount of $Et_3Al(l)$ ($\approx 50\%$ in excess of stoichiometric) was drawn up into a hypodermic syringe fitted with a long needle (the needle was long enough to extend to the liquid surface during introduction of the Et_3Al into the calorimeter). After closing the needle tip with a small piece of rubber, the syringe was weighed and placed in a Dewar along with a thermometer. Calorimeter temperature readings were taken at half-minute intervals before and after the introduction of the Et_3Al. The reaction was usually completed within five minutes as shown by a steady rate of temperature fall. The temp. rise for the experiment (5—7°) was determined from a temp. vs. time plot (the initial temp was corrected for the difference in temp. between the calorimeter and the Et_3Al).

The heat liberated was calculated from the temp. rise and the heat capacities of the calorimeter, the hexadecane, the reaction products, and the excess Et_3Al. Before dividing by the gfw's of $Et_2AlX(l)$ formed, the heat liberated was converted to a solvent-free basis by making appropriate corrections for the heats of solution of reactants, products and the excess Et_3Al. Since the heat capacities of the products were used, rather than those of the reactants, the value obtained for the ΔH of reaction was taken as applying at the initial temp. of the reaction ($25.0 \pm 1.5°$).

Experiments of the type $Et_3Al(l) + EtAlX_2(l) \rightarrow 2\ Et_2AlX(l)$ were performed similarly except that both reactants were added as liquids. About 0.015 gfw $EtAlX_2$ and a 50% excess of Et_3Al were used. As might be expected, these reactions were completed much faster than the reactions of the first type. The calculation of results was also similar, appropriate corrections again being made for heats of solution.

For experiments of the type $Et_2AlX(l) + EtAlX_2(l) \rightarrow Et_3Al_2X_3(l)$, ≈ 0.045 gfw $EtAlX_2$ was premixed in the calorimeter with hexadecane (≈ 30 ml). A small quantity (≈ 0.003 gfw) of Et_2AlX was also added to eliminate any traces of AlX_3 that might be present in the $EtAlX_2$. Subsequently ≈ 0.045 gfw Et_2AlX (to which ≈ 0.003 gfw $EtAlX_2$ had been added to eliminate any traces of Et_3Al) was added and the temp. rise measured. In the calculations, account was taken of the $Et_3Al_2X_3$ already present, both in the calorimeter and in the syringe, before the main mixing. Appropriate corrections were made for heats of solution.

Duplicate values of $-\Delta H$ obtained for $\frac{2}{3}$ $Et_3Al(l) + \frac{1}{3} AlX_3(c) \rightarrow Et_2AlX(l)$ are 5.28 and 5.37 for $X = Cl$; 7.21 and 7.36 for $X = Br$; 5.77 and 5.91 for $X = I$. Duplicate values for $Et_3Al(l) + EtAlX_2(l) \rightarrow 2\ Et_2AlX(l)$ are 9.36 and 9.52 for $X = Cl$; 9.43 and 9.55 for $X = Br$; 8.56 and 8.75 for $X = I$. The "relative deviation" for each pair was calculated as d/m, where d = deviation from the mean (half the range) and m = mean value. The root-mean-square of the six relative deviation values was evaluated as $r = 0.0096$. The uncertainty assigned to each mean value was $\pm 2rm$. Duplicate values of $-\Delta H$ obtained for $Et_2AlX(l) + EtAlX_2(l) \rightarrow Et_3Al_2X_3(l)$ are 0.53 and 0.56 for $X = Cl$; 0.57 and 0.61 for $X = Br$. An uncertainty of ±0.05, determined by a similar procedure, was assigned to each mean value. When equations representing separate processes were added or subtracted, the uncertainty for the resulting equation was obtained by summing the squares of the individual uncertainties and extracting the square root.

The heat of solution of excess $Et_3Al(l)$ in hexadecane for each experiment was calculated from the results of earlier work [12]. Other heats of solution required were determined in separate experiments. $AlCl_3(c)$ and $AlI_3(c)$ had negligible heats of solution since they were almost insoluble. $AlBr_3(c)$, however, dissolved to a considerable extent, hence its heat of solution was appreciable. Referring to the equation $\Delta H_m = AX_a(1 - X_a)$, in which ΔH_m = molar heat of mixing and X_a = mole fraction of aluminum compound (monomeric basis), "A" values at 25 ± 1.5° were determined as follows: $Et_2AlCl(l)$, 206; $Et_2AlBr(l)$, 234; $Et_2AlI(l)$, 270; $EtAlCl_2(l)$, 780; and $EtAlBr_2(l)$, 540. These values were determined in dilute solution, of course, and hence do not represent the entire composition range.

Heat capacity data

The specific heat of n-hexadecane was taken from ref. 45. The specific heats of $Et_3Al(l)$, $Et_2AlCl(l)$ and $EtAlCl_2(l)$ were determined in this laboratory [37]. The specific heats of the remaining liquid alkylaluminum halides were estimated by the method of Johnson and Huang [46] used in conjunction with published values [32] for the liquid aluminum halides.

References

1 S. Pawlenko, Chem. Ber., 102 (1969) 1937.
2 J.D. Cox and G. Pilcher, Thermochemistry of Organic and Organometallic Compounds, Academic Press, London, 1970.
3 T.L. Allen, J. Chem. Phys., 31 (1959) 1039.
4 H.A. Skinner, J. Chem. Soc., (1962) 4396.
5 J.P. McCullough and W.D. Good, J. Phys. Chem., 65 (1961) 1430.
6 F.D. Rossini, K.S. Pitzer, R.L. Arnett, R.M. Braun and G.C. Pimentel, Selected values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds, Carnegie Press, Pittsburgh, Pa., 1953 and supplements.
7 L.H. Long and R.G.W. Norrish, Phil. Trans. Roy. Soc. London, Ser. A, 241 (1949) 587.
8 W.H. Johnson, M.V. Kilday and E.J. Prosen, J. Res. Nat. Bur. Stand. Sect A, 65 (1961) 215.
9 A.E. Pope and H.A. Skinner, J. Chem. Soc., (1963) 3704.
10 J.V. Davies, A.E. Pope and H.A. Skinner, Trans. Faraday Soc., 59 (1963) 2233.
11 W.F. Lautsch, A. Tröber, W. Zimmer, L. Mehner, W. Linck, H.M. Lehmann, H. Brandenburger, H. Körner, H.J. Metzschker, K. Wagner and R. Kaden, Z. Chem., 3 (1963) 415.
12 M.B. Smith, J. Phys. Chem., 71 (1967) 364.
13 M.B. Smith, J. Organometal. Chem., 22 (1970) 273.
14 M.B. Smith, J. Organometal. Chem., 46 (1972) 31.

15 M.B. Smith, J. Organometal. Chem., 70 (1974) 13.
16 P.A. Fowell, Ph. D. Thesis, University of Manchester, 1961.
17 C.T. Mortimer and P.W. Sellers, J. Chem. Soc. (1963) 1978.
18 V. Fic, Chem. Prum., 16 (1966) 607.
19 A. Troeber and C. Stricker, Wiss. Z. Tech. Hochsch. Chem. Leuna — Merseburg, 8 (1966) 34.
20 Y.K. Shaulov, G.O. Shmyreva and V.S. Tubanskaya, Russ. J. Phys. Chem., 39 (1965) 51.
21 G.O. Shmyreva, G.B. Sakharovskaya, A.F. Popov, N.N. Korneev and A.A. Smolyaninova, Russ. J. Phys. Chem., 45 (1971) 260.
22 Y.K. Shaulov, V.S. Tubyanskaya, E.V. Evstegneeva and G.O. Shmyreva, Russ. J. Phys. Chem., 38 (1964) 967.
23 S. Pawlenko, Chem. Ber., 100 (1967) 3591.
24 H.A. Skinner, Advan. Organometal. Chem., 2 (1964) 97.
25 E.G. Hoffmann and W. Tornau, Z. Anal. Chem., 188 (1962) 321.
26 W.L. Everson and E.M. Ramirez, Anal. Chem., 37 (1965) 806.
27 G.E. Coates and K. Wade, Organometallic Compounds, Volume I, 3rd Ed., Methuen and Co. Ltd., London, 1967.
28 D.D. Wagman, W.H. Evans, V.B. Parker, I. Halow, S.M. Bailey and R.H. Schumm, NBS Technical Note 270—3, National Bureau of Standards, Washington, D.C., 1968.
29 W.F. Stack, G.A. Nash and H.A. Skinner, Trans. Faraday Soc., 61 (1965) 2122.
30 E.I. Larikov, A.F. Zhigach, A.F. Popov, T.N. Kulikovskaya and N.V. Vladytskaya, Khim. Prom., 40 (1964) 171.
31 E.G. Hoffmann, Ann. Chem., 629 (1960) 104.
32 D.R. Stull and H. Prophet, JANAF Thermochemical Tables, 2nd Edn., NSRDS — NBS37, 1971, and supplements.
33 G.A. Nash, H.A. Skinner and W.F. Stack, Trans. Faraday Soc., 61 (1965) 640.
34 H.O. Pritchard, Chem. Rev., 52 (1953) 529.
35 K. Hartley, H.O. Pritchard and H.A. Skinner, Trans. Faraday Soc., 46 (1950) 1019; 47 (1951) 254.
36 Y.K. Shaulov and G.O. Shmyreva, Russ. J. Phys. Chem., 42 (1968) 1008.
37 M.B. Smith, unpublished results.
38 J. Brandt and E.G. Hoffmann, Brennst. Chem., 45 (1964) 200.
39 T. Mole and E.A. Jeffery, Organoaluminum Compounds, Elsevier, Amsterdam, 1972.
40 D.R. Stull, E.F. Westrum, Jr. and G.C. Sinke, The Chemical Thermodynamics of Organic Compounds, Wiley, New York, 1969.
41 M.B. Smith and G.E. Bass, J. Chem. Eng. Data, 8 (1963) 342.
42 R.C. Wilhoit and B.J. Zwolinski, Handbook of Vapor Pressures and Heats of Vaporization of Hydrocarbons and Related Compounds, Thermodynamics Research Center, Dept. of Chemistry, Texas A and M University, 1971.
43 J.B. Greenshields and F.D. Rossini, J. Phys. Chem., 62 (1958) 271.
44 E. Morawetz, J. Chem. Thermodynam., 4 (1972) 145.
45 J.F. Messerly, G.B. Guthrie, S.S. Todd and H.L. Finke, J. Chem. Eng. Data, 12 (1967) 338.
46 A.I. Johnson and C.J. Huang, Can. J. Technol., 33 (1955) 421.
47 S.W. Benson, F.R. Cruickshank, D.M. Golden, G.R. Haugen, H.E. O'Neal, A.S. Rodgers, R. Shaw and R. Walsh, Chem. Rev., 69 (1969) 279.