Standard Enthalpy of Formation of Triethylaluminum

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Summary: The standard enthalpy of formation of liquid $AlEt_3$ was determined from the experimental enthalpy of reaction of this compound with acetylacetone in toluene. The result was then used to assess the available thermochemical data for other trialkylaluminum compounds.

Although the industrial importance of organoaluminum compounds has been growing over the past 30 years, the available thermochemical data for these substances are still affected by considerable uncertainties. For instance, values reported by different authors for the enthalpy of formation of $AlEt_3$ differ by as much as 83 kJ/mol and for $Al(\textit{i}\text{-}Bu)_3$ as much as 96 kJ/mol (Table I). Even values for the series of molecules R_2AlCl (R = alkyl) measured by the same author[1] vary randomly with increasing alkyl chain length, which indicates inconsistency in the results.[2] The difficulties in handling and purifying the samples of these compounds can be partially responsible for the discrepancies, but the choice of the thermochemical method to determine their enthalpies of formation is also important. Combustion calorimetry, for example, is not considered to be the best method to solve this problem.[3] Reaction-solution calorimetry, on the other hand, requires the use of fast reactions with very high yields, in additon to special precautions regarding the absence of moisture and oxygen. Apparently, rapid and high-yield reactions should not be a problem in the case of aluminum alkyls, since they are extremely reactive. Yet, it is precisely their high reactivity that raises difficulties in finding a suitable reaction for probing their energetics in a calorimeter.

We have found that reaction 1 meets the required conditions to evaluate the enthalpies of formation of aluminum alkyls, and we have used it to determine the standard enthalpy of formation of the key compound $AlEt_3$.

$$AlEt_3(l) + 3Hacac(soln) \rightarrow Al(acac)_3(soln) + 3EtH(g/soln) \quad (1)$$

Experimental Section

All operations were carried out under vacuum or under an inert atmosphere, and all solvents were degassed before use.

Materials. The purity of $AlEt_3$ (Aldrich) was claimed to be better than 93%. This sample was used without further purification (see discussion below). According to the manufacturers, typical impurities are $AlBu_3$ (5%), $Al(\textit{i}\text{-}Bu)_3$ (0.6%), AlH_3 (0.4%), $AlMe_3$ (0.2%), and other species (0.8%). A very concentrated ^1H NMR spectrum in toluene-d_8 revealed only very minor impurities, and a ^{13}C NMR spectrum showed that the amount of $AlBu_3$ is less than 5%. A minor amount of $Al(\textit{i}\text{-}Bu)_3$ was also detected. Positive and negative ion mass spectra showed that chlorine or oxygen derivatives of aluminum alkyls were not present in the Aldrich sample. ^1H NMR spectra were recorded with a Bruker SY80-FT spectrometer and were referenced to TMS. ^{13}C NMR spectra were obtained with a Varian 300 spectrometer. The mass spectra were recorded with an Extrel 2001 FT-ICR mass spectrometer.

Table I. Experimental Enthalpies of Formation of Aluminum Trialkyls (kJ/mol)[a]

molecule	ΔH_f^0 (l) [method/ref][b]	molecule	ΔH_f^0 (l) [method/ref][b]
$AlMe_3$	−144.4 ± 11.1* [RSC/10][c]	$AlPr_3$	−322.2 ± 4.6 [SB/16][d]
	−120.1 ± 10.0 [SB/11][d]		−282 ± 15* [SB/17][c]
	−151.9 [SB/12][e]	$AlBu_3$	−372.4 ± 5.7* [SB/16][c]
$AlEt_3$	−187.3 ± 5.1* [RSC/this work]	$Al(\textit{i}\text{-}Bu)_3$	−388.3 ± 7.7 [SB/16][c]
	−154 ± 19 [RSC/13]		−292 ± 30* [SB/18][d]
	−173.2 [SB/14][f]		
	−217.1 ± 2.2 [SB/15][d]		
	−236.8 ± 3.1 [SB/16][c]		

[a] Enthalpies of formation refer to the "real liquids", i.e. the equilibrium monomer–dimer mixtures (see text). Values are given per mole of monomer. [b] Legend: RSC = reaction-solution calorimetry; SB = static bomb combustion calorimetry. Reaction-solution results were recalculated by using more recent auxiliary data. Selected (but not necessarily accurate) values are indicated by an asterisk (see text for discussion). [c] Quoted from: Pilcher, G.; Skinner, H. A. In *The Chemistry of the Metal-Metal Bond*; Hartley, F. R., Patai, S., Eds.; Wiley: New York, 1982; Chapter 2. [d] Quoted from: Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic: London, New York, 1970. [e] Quoted from ref 2. [f] Quoted from: Tel'noi, V. I.; Rabinovich, I. B. *Russ. Chem. Rev.* (*Engl. Transl.*) **1980**, *49*, 603.

Acetylacetone (BDH) was predried with phosphorus pentoxide for 3 days and then distilled over fresh P_2O_5 and kept in a glovebox.

$Al(acac)_3$ was prepared by the following method: $AlEt_3$ (800 mg, 7.08 mmol) was added, inside a glovebox (water and oxygen contents lower than 5 ppm), to ca. 100 mL of toluene at room temperature. An excess of Hacac (3.100 g, 30.96 mmol) was slowly added with stirring, and the final mixture was allowed to react. The solution was evaporated to dryness, yielding a white powder identified with $Al(acac)_3$ by ^1H NMR and elemental analysis (C and H elemental analyses were made with a Perkin-Elmer automatic analyzer). Anal. Calcd for $C_{15}H_{21}O_6Al$: C, 55.55; H, 6.53. Found: C, 55.95; H, 6.90.

Toluene was predried over 4-Å molecular sieves and distilled from sodium, potassium, and benzophenone. Toluene-d_8 and benzene-d_6 (used to run some NMR spectra) were dried over sodium and distilled.

Calorimetry. The anaerobic reaction-solution calorimeter and the experimental procedure used were described elsewhere.[4] In each of six independent experiments, a sealed glass ampule containing 0.12–1.2 mmol of this substance was broken in 140 mL of a 0.0534 M or a 0.0356 M solution of acetylacetone in toluene. These concentrations ensured a stoichiometric excess of Hacac relative to triethylaluminum. All measurements,

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(1) Pawlenko, S. *Chem. Ber.* **1969**, *102*, 1937.

(2) Smith, M. B. *J. Organomet. Chem.* **1974**, *76*, 171.

(3) Pilcher, G. In *Energetics of Organometallic Species*; Martinho Simões, J. A., Ed.; Kluwer: Dordrecht, The Netherlands, 1992.

(4) Leal, J. P.; Pires de Matos, A.; Martinho Simões, J. A. *J. Organomet. Chem.* **1991**, *403*, 1.

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including the auxiliary enthalpies of solution, were made at 298 K, and the results are averages of at least five runs. The errors presented are twice the standard deviation of the mean in each case.

Results and Discussion

One important advantage of reaction 1, besides being rapid and quantitative, is that it produces $Al(acac)_3$, whose enthalpy of formation is well established as −1792.9 ± 1.9 kJ/mol,[5] allowing an accurate determination of $\Delta H_f^0(AlEt_3,l) = -187.3 \pm 5.1$ kJ/mol through eq 2. Here, ΔH_r

$$\Delta H_f^0(AlEt_3,l) = -\Delta H_r - 3\Delta H_{d1} + \Delta H_{d2} + (3 \times 0.8)\Delta H_{d3} + \Delta H_f^0[Al(acac)_3,c] + 3\Delta H_f^0(EtH,g) - 3\Delta H_f^0(Hacac,l) \quad (2)$$

(−587.0 ± 2.9 kJ/mol) is the enthalpy of reaction 1, ΔH_{d1} (−0.4 ± 0.6 kJ/mol) is the enthalpy of solution of acetylacetone[6] in toluene, ΔH_{d2} (13.7 ± 0.9 kJ/mol) is the enthalpy of solution of aluminum tris(acetylacetonate) in toluene containing stoichiometric amounts of Hacac, and ΔH_{d3} (−8.91 kJ/mol)[7] represents the enthalpy of solution of ethane in toluene. It is assumed that about 80% of the ethane formed stays in solution.[8]

The value calculated above for the enthalpy of formation of $AlEt_3$ (−187.3 ± 5.1 kJ/mol) refers to the equilibrium mixture dimer/monomer, which, according to Smith,[2,9] contains a negligible amount of monomer at 298 K (ca. 0.1%). Therefore, the enthalpy of formation of the "real liquid"[2] should rather be considered as $\Delta H_f^0(Al_2Et_6,l) = -374.6 \pm 10.2$ kJ/mol. The enthalpy of formation of the monomer can, on the other hand, be derived from the enthalpy of reaction 3 (70.8 ± 1.0 kJ/mol).[9] One obtains $\Delta H_f^0(AlEt_3,l,monomer) = -151.9 \pm 5.1$ kJ/mol.

$$(AlEt_3)_2(l) \rightarrow 2AlEt_3(l) \quad (3)$$

The available literature values of the enthalpies of formation of aluminum trialkyls (dimer–monomer equilibrium mixtures) are summarized in Table I (per mole of AlR_3), together with the experimental methods used to determine them.[10–18] In the cases of $AlMe_3$, $AlPr_3$, and $AlBu_3$ the liquids contain very small amounts of monomers at 298 K (ca. 0.007%, 0.5%, and 0.8%, respectively),[19,20] so that the enthalpies of formation of the dimers, in kJ/mol of dimer, can be calculated by multiplying those values by 2 (the errors resulting from this approximation are smaller than the uncertainties assigned to the experimental enthalpies of formation). The data for the monomers can then be obtained as described above for triethylaluminum, since the enthalpies of reaction equivalent to reaction 3 were measured by Smith (kJ/mol): 81.2 ± 1.3 ($AlMe_3$),[19] 64.5 ± 0.8 ($AlPr_3$),[20] and 62.8 ± 0.6 ($AlBu_3$).[20] The results are displayed in Table II, together with the gas-phase enthalpies of formation of the monomers[19–21] and the mean aluminum–alkyl bond dissociation enthalpies. Also included are the data for $Al(i\text{-}Bu)_3$. In this case the monomer is the dominant component of the real liquid (about 74% at 298 K),[21] so that a correction had to be made to derive its enthalpy of formation.

Table II. Enthalpies of Formation and Bond Enthalpy Data for Monomeric Aluminum Trialkyls (kJ/mol)

molecule	$\Delta H_f^0(l)$	$\Delta H_f^0(g)^a$	$\bar{D}(Al\text{–}alkyl)^b$
$AlMe_3$	−104 ± 11	−81 ± 11	283 ± 4
$AlEt_3$	−152 ± 5	−112 ± 5	265 ± 5
$AlPr_3$	−250 ± 15	−197 ± 15	270 ± 7
$AlBu_3$	−341 ± 6	−275 ± 6	274 ± 8
$Al(i\text{-}Bu)_3$	−288 ± 36	−226	252

[a] Enthalpies of vaporization of the monomers are given in ref 2. [b] $\Delta H_f^0(Al,g) = 326.4 \pm 4.0$ kJ/mol.[22] Enthalpies of formation of alkyl radicals are taken from ref 26.

Since we believe that our value for the enthalpy of formation of triethylaluminum is quite reliable (see comments below), it can help us to assess the remaining data in Tables I and II. The disagreement with the static-bomb combustion values in Table I is not surprising, but a discrepancy with another reaction-solution calorimetry value is also observed. This result, however, relies on the measured enthalpy of reaction 4, −647.3 ± 6.3 kJ/mol,[13]

$$AlEt_3(l) + 3H_2O(g) \rightarrow Al(OH)_3(am) + 3EtH(g) \quad (4)$$

and on the NBS value for the enthalpy of formation of amorphous aluminum hydroxide, $\Delta H_f^0[Al(OH)_3,am] = -1276$ kJ/mol.[22] This value for the enthalpy of formation of $Al(OH)_3$ is probably inaccurate and responsible for the discrepancy between our value of $\Delta H_f^0(AlEt_3,l)$ and the one reported by Fowell (Table I). If the published enthalpy of reaction 4 is accepted, $\Delta H_f^0[Al(OH)_3,am]$ can be recalculated as −1308.6 ± 8.2 kJ/mol by using our result for $\Delta H_f^0(AlEt_3,l)$ in Table I. This recalculated value is closer to another recommended elsewhere, −1293.5 ± 1.2 kJ/mol.[23]

Smith has made a detailed discussion of enthalpies of formation of monomeric and dimeric aluminum trialkyls and suggested a method to estimate their values, by assuming that the enthalpy of reaction 5 is independent

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[5] $\Delta H_f^0[Al(acac)_3,c] = -1792.9 \pm 1.9$ kJ/mol is the average of the results reported by: (a) Cavell, K. J.; Pilcher, G. *J. Chem. Soc., Faraday Trans. 1* **1977**, *73*, 1590. (b) Hill, J. O.; Irving, R. J. *J. Chem. Soc. A.* **1966**, 971.

[6] The enthalpy of formation of liquid acetylacetone was taken as $\Delta H_f^0(Hacac,l) = -425.5 \pm 1.0$ kJ/mol. This value corresponds to the keto (18.6%) + enol (81.4%) equilibrium mixture at 298 K (see: Hacking, J. M.; Pilcher, G. *J. Chem. Thermodyn.* **1979**, *11*, 1015).

[7] Wilhelm, E.; Battino, R. *Chem. Rev.* **1973**, *73*, 1.

[8] It is assumed that the amount of ethane in toluene is identical with the amount of ethylene under similar conditions (Calhorda, M. J.; Carrondo, M. A. A. F. de C. T.; Dias, A. R.; Galvão, A. M.; Garcia, M. H.; Martins, A. M.; Minas da Piedade, M. E.; Pinheiro, C. I.; Romão, C. C.; Martinho Simões, J. A.; Veiros, L. F. *Organometallics* **1991**, *10*, 483). These gases have approximately the same values for solubility, entropy of solution, and enthalpy of solution, in toluene.[7] $\Delta H_f^0(EtH,g) = -83.8 \pm 0.4$ kJ/mol (Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds*; Chapman and Hall: New York, 1986).

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[19] Smith, M. B. *J. Organomet. Chem.* **1972**, *46*, 31.

[20] Smith, M. B. *J. Organomet. Chem.* **1974**, *70*, 13.

[21] Smith, M. B. *J. Organomet. Chem.* **1970**, *22*, 273. The enthalpy of dissociation of the dimer is 34.1 ± 0.5 kJ/mol.

[22] Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Halow, I.; Bailey, S. M.; Churney, K. L.; Nuttall, R. L. The *NBS Tables of Chemical Thermodynamic Properties. J. Phys. Chem. Ref. Data* **1982**, *11*, Suppl. 2.

[23] Gurvich, L. V., et al. *Thermodynamic Properties of Pure Substances* (Russian Edition); Nauka: Moscow, 1981; Vol. 3, Part 1.

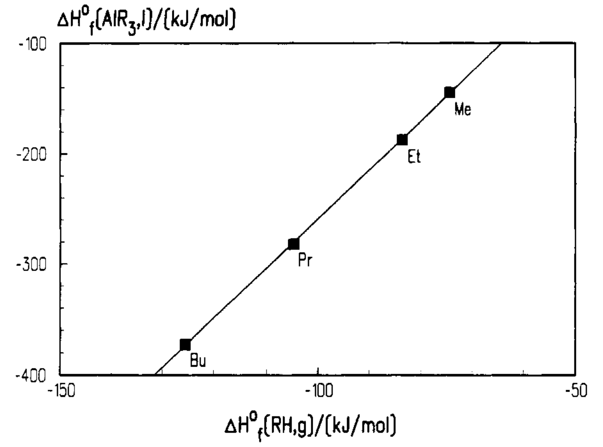

Figure 1. Enthalpies of formation of liquid (dimeric) aluminum alkyls plotted against the enthalpies of formation of gaseous alkanes.

of the alkyl group R.[2] Although the assumption was not

$$Al(c) + 3RMe(g) \rightarrow Al(CH_2R)_3(g) + 1.5H_2(g) \quad (5)$$

confirmed by the older values in Table II, Smith decided to anchor all his estimates on the result obtained for $AlMe_3$, which is recalculated as $\Delta H(5) = 141.9 \pm 11.2$ kJ/mol.[24] Our new value for $AlEt_3$ leads to $\Delta H(5) = 139.2 \pm 5.2$ kJ/mol, thus supporting Smith's choice and indicating that the experimental data for $AlMe_3$ are also reliable. One may therefore use the enthalpy of reaction 5 to calculate the enthalpy of formation of gaseous monomeric AlR_3 and then take the available enthalpies of vaporization of the monomers and the enthalpies of dissociation of the dimers, as well as the equilibrium compositions of the "real liquids", to predict enthalpies of formation of other aluminum trialkyls. This is a simple exercise and will not be performed here. It is only stressed that, for example, the "best" data for $AlPr_3$ and $AlBu_3$ (Table I) yield $\Delta H(5)$ values that are 23 and 38 kJ/mol lower than the constant mentioned above (ca. 140 kJ/mol). Their inaccuracy could of course be expected, since they were obtained by static bomb combustion calorimetry—the same method that afforded large discrepancies in $\Delta H_f^0(AlEt_3,l)$.

If one uses another method to assess the data, which consists of plotting $\Delta H_f^0(AlR_3,l/g)$ against $\Delta H_f^0(RH,rs/g)$,[24,25] the inconsistencies are not so evident. In fact, Figures 1 and 2 and eqs 6 and 7, involving the selected values from Tables I ("real liquids") and II (gaseous monomers), respectively, show excellent linear correlations ($r = 0.9999$ and 0.9996).

$$\Delta H_f^0(AlR_3,l) = (4.457 \pm 0.039)\Delta H_f^0(RH,rs) + (186.4 \pm 3.9) \quad (6)$$

$$\Delta H_f^0(AlR_3,g) = (3.819 \pm 0.073)\Delta H_f^0(RH,g) + (204.7 \pm 7.2) \quad (7)$$

What method should we rely on, Smith's or the above correlations? It can be easily shown that they are mathematically equivalent—the constancy of $\Delta H(5)$ and the linear plot of $\Delta H_f^0(AlR_3,g)$ versus $\Delta H_f^0(RH,g)$ both imply that the aluminum–alkyl mean bond dissociation enthalpies parallel the carbon–hydrogen bond dissociation enthalpies in the alkanes. In the case of eq 7, however, this would hold only if the slope were equal to the number of alkyl groups bonded to the aluminum. (The slope in eq 6 is quite large, but we could try to justify it by invoking the dimeric structure in the liquid.)

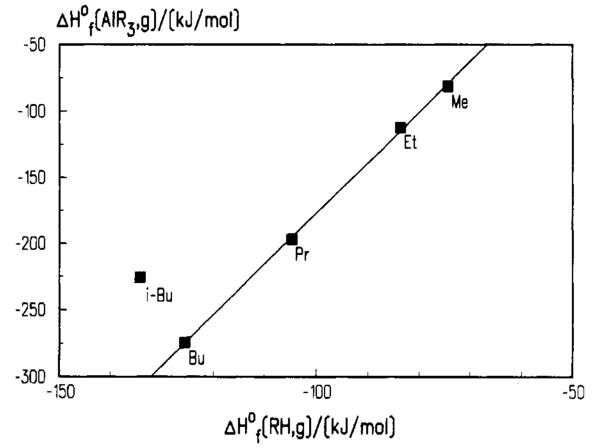

Figure 2. Enthalpies of formation of gaseous (monomeric) aluminum alkyls plotted against the enthalpies of formation of gaseous alkanes.

From the many examples shown in the literature,[25,26] there is no apparent reason why the above trend for the bond dissociation enthalpies should not be observed for AlR_3. The fact that it is not is shown by the large slope of eq 7 and by the $\bar{D}$(Al–R) values in Table II, e.g. $\bar{D}(Al–Et) - \bar{D}(Al–Bu) = -9$ kJ/mol whereas $D(Et–H) - D(Bu–H) = 3$ kJ/mol.[27] In conclusion, we strongly believe that the quality of the correlations in Figures 1 and 2 is fortuitous and that the best method to estimate reliable values of enthalpies of formation of monomeric aluminum trialkyls is simply to draw a line of slope 3 from the value reported in this paper for $\Delta H_f^0(AlEt_3,g)$. Incidentally, this slope is approximately observed when the values for $\Delta H_f^0(AlMe_3,g)$ and $\Delta H_f^0(AlEt_3,g)$ in Table II (the only ones which are likely to be accurate) are plotted against the enthalpies of formation of methane and ethane. This can of course be fully checked by probing the thermochemistry of the propyl and butyl analogs by measuring their reaction with acetylacetone, but the difficulties of handling and purifying these substances prevent us from attempting these experiments.

A final comment on the purity of the sample used in our thermochemical measurements should be made. According to the previous analysis, the presence of $AlBu_3$ as a major impurity would have a negligible effect on the value recommended for the enthalpy of formation of $AlEt_3$ (the enthalpy of reaction 1 for $AlBu_3$ would be identical with the one measured for the ethyl analogue).

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[24] The enthalpies of formation of alkanes were taken from the second reference given in ref 8. "rs" indicates "reference state", i.e. the most stable state of a compound at 298 K and 1 bar.

[25] See: Martinho Simões, J. A. In *Energetics of Organometallic Species*; Martinho Simões, J. A., Ed.; Kluwer: Dordrecht, The Netherlands, 1992, and references cited therein.

[26] See, for example: Martinho Simões, J. A.; Beauchamp, J. L. *Chem. Rev.* **1990**, *90*, 629 and references cited therein.

[27] This looks like a small discrepancy, but it leads to a difference of 36 kJ/mol in the enthalpy of formation of $AlBu_3$.