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"Heats of Formation and Bond Energies of Organo-metallic Compounds,  
n-Butyl-lithium,  
Trimethylaluminium and Triethylaluminium."

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Abstract

The heats of hydrolysis of n-butyl-lithium and triethylaluminium have been measured, using a Dewar-vessel calorimeter, and the data used to calculate the values  $\Delta H_f^\circ(\text{n-BuLi, liq.}) = 31.4 \pm 0.7$  kcal./mole, and  $\Delta H_f^\circ(\text{Et}_3\text{Al, liq.}) = -36.5 \pm 5.5$  kcal./mole. Using a rotating-bomb calorimeter, the heat of reaction of trimethylaluminium and acetic acid has been determined. The heat of solution of aluminium triacetate in hydrochloric acid has also been obtained. These measurements are used to calculate the values  $\Delta H_f^\circ(\text{Me}_3\text{Al, liq.}) = -36.1 \pm 1.6$  kcal./mole and  $\Delta H_f^\circ[(\text{CH}_3\text{COO})_3\text{Al, cryst.}] = -451.8 \pm 0.8$  kcal./mole.

The mean bond dissociation energies  $\bar{D}(\text{Li-Bu}) = 54 \pm 9$ ,  $\bar{D}(\text{Al-Et}) = 56.8 \pm 4.0$ , and  $\bar{D}(\text{Al-Me}) = 64.5 \pm 2.0$  kcal./mole are derived.

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## Introduction

There is very little information about the strength of metal-carbon bonds in the organo-metallic compounds  $MR_n$  where M is one of the lighter metals lithium, beryllium, or aluminium and R is an alkyl radical. The mean bond dissociation energy  $\bar{D}(M-C)$  is an expression of the strength of these bonds and is readily calculated from the relation  $\bar{D}(M-C) = \Delta H_f^\circ(R, g.) + \frac{1}{n}\Delta H_f^\circ(M, g.) - \frac{1}{n}\Delta H_f^\circ(MR_n, g.)$ .

The object of the work carried out has been to determine heats of formation,  $\Delta H_f^\circ$ , of some of these organo-metallic compounds, in order to obtain more information about the strengths of metal-carbon bonds. Three compounds have been studied in this investigation, n-butyl-lithium, triethylaluminium and trimethylaluminium.

Accurate determination of the heats of formation of these compounds is difficult because of their high reactivity. There are few reactions which are stoichiometrically well-defined and which are also suitable for thermochemical study. Hydrolysis under controlled conditions has been successful for n-butyl-lithium and for trimethylaluminium, though less so for triethylaluminium.

The heats of hydrolysis, at constant pressure, of n-butyl-lithium and triethylaluminium with gaseous water have been measured using a Dewar-vessel calorimeter, which is shown diagrammatically on page 27. For trimethylaluminium, which is considerably more reactive, this method proved unsatisfactory, but the heat of reaction with acetic acid, at constant volume in a rotating-bomb calorimeter, has been measured. This apparatus is shown on pages 28 and 29. One of the products of this reaction is aluminium triacetate, and as the heat of formation of this compound was not available, it was determined from measurement of its heat of solution in hydrochloric acid.

The thermochemical studies of the three organo-metallic compounds, n-butyl-lithium, triethylaluminium and trimethylaluminium differ in a number of aspects. The details of these investigations are presented, therefore, in three separate sections which follow.

### Publications

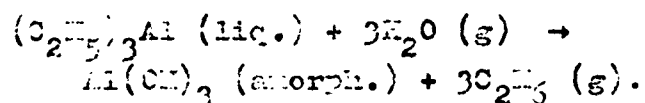
Parts of this work have been, or are being published as follows:

1. Heats of Formation and Bond Energies. Part V.  
n-Butyl-lithium.  
By P.A. Powell and C.T. Mortimer.  
J. Chem. Soc., 1961, 3793.
2. Heats of Formation and Bond Energies. Part IX.  
Trimethylaluminium and Aluminium triacetate.  
By P.W. Sellers and C.T. Mortimer.  
J. Chem. Soc., in press.
3. Heats of Formation and Bond Energies.  
Triethylaluminium.  
By P.A. Powell and C.T. Mortimer.  
To be published.

Triethylaluminium

By P.A. Fowell and C.T. Mortimer.

The heat of hydrolysis of triethylaluminium has been measured. A known weight of water vapour was allowed to react with an excess of liquid triethylaluminium in an isothermal calorimeter at 25°C. The measured heat  $\Delta H = -154.3 \pm 2.0$  kcal./mole, is taken to refer to the reaction



The heat of formation  $\Delta H_f^\circ [(\text{C}_2\text{H}_5)_3\text{Al, liq.}] = -36.5 \pm 5.5$  kcal./mole is calculated.

Triethylaluminium is highly reactive and many of its reactions are not well defined, unless carried out under carefully controlled conditions. Thus, degradative oxidation (combustion) produces a mixture containing a number of different products. In addition, triethylaluminium is difficult to purify, so that the heat of combustion, which will be large, would be subject to a large absolute error, due to such impurities. A reaction in which the products are more well defined and which is accompanied by a small heat change would, therefore, be more suitable.

Such a reaction is that between triethylaluminium and iodine, in an inert solvent at room temperature. There is a quantitative yield of aluminium triiodide and ethyl iodide. However, to keep a comparatively large volume of solvent, in which the iodine is dissolved, free from water to avoid a competing hydrolysis reaction presents considerable experimental difficulties.

Hydrolysis of triethyl aluminium in an excess of

water has the advantage that the final state of the aluminium content would be as an aqueous solution, which would be a thermochemically well-defined state. However, hydrolysis in excess water is violent and a number of hydrocarbons other than ethane are produced under these conditions. Since facilities were not available to carry out analysis of the gases produced this approach was rejected.

Instead, an attempt has been made to measure the heat of hydrolysis under more controlled conditions, by passing a known weight of water vapour, in a stream of nitrogen as carrier gas, into liquid triethylaluminium. It was not possible to analyse the gaseous products, but it is reasonable to assume that under these mild conditions, it consisted entirely of ethane. On this assumption it has been possible to calculate the heat of formation of triethylaluminium.

#### EXPERIMENTAL

Compounds.- Triethylaluminium was supplied by Mr. E.R.A. Forshaw of Carrington Research Laboratory, Petrochemicals Ltd., Manchester, U.K. The sample contained triethylaluminium, 95.3%, diethylaluminium hydride and ethylaluminium dihydride, 2.9%, aluminium triethoxide, 0.8%, and tributylaluminium, 0.9%. It was found to be difficult to purify the sample further.

Calorimeter.- The calorimeter used to study the heat of hydrolysis of triethylaluminium was a modified form of that described previously by Pedley, Skinner and Chernick.<sup>1</sup>

The reaction vessel was charged with about 10 ml. of triethylaluminium in an atmosphere of dry nitrogen. The calorimeter was assembled and allowed to reach

thermal equilibrium. A stream of dry, oxygen-free nitrogen was passed through a glass spiral immersed in a bath thermostatted at 25°C, and was allowed to bubble through the liquid triethylaluminium for a pre-reaction period. The nitrogen stream was saturated with water vapour, by bubbling through a 'water-saturator', a weighed vessel containing liquid water, and allowed to pass into the reaction vessel for a short time. Finally the stream of dry nitrogen was resumed for a post-reaction period. The amount of water which reacted was calculated from the loss of weight of the 'water-saturator' vessel.

It was found necessary to correct this weight because having weighed the water-saturator and set up the apparatus a small amount of water vaporised and condensed along the walls of the nitrogen inlet-tube, at the point where it enters the calorimeter. This water was normally swept into the calorimeter during the first few minutes of the pre-reaction period. The 'vaporised water correction' was normally 3 to 4% of the total weight of water evaporated from the water-saturator.

A second correction was applied, in this case to the observed temperature rise of the calorimeter. In the process of connecting the water-saturator to the system, after weighing, a small amount of air found its way into this part of the apparatus. The first few ml. of nitrogen which passed through the water-saturator displaced this air, the oxygen content of which reacted immediately with the triethyl aluminium. Following the temperature-time curve it was quite easy to distinguish this reaction from the hydrolysis which followed immediately. This 'oxygen correction' normally reduced the observed temperature rise by about 3%. These two corrections act in an opposite sense and tend to cancel each other.

Typical results of a series of about twenty runs

are shown in Table 1.

Here  $\Delta H$  is taken to refer to reaction (1) below. The uncertainty quoted is twice the standard deviation. The error introduced by the impurities in the triethylaluminium is much less than the uncertainty we have quoted for the heat of hydrolysis.

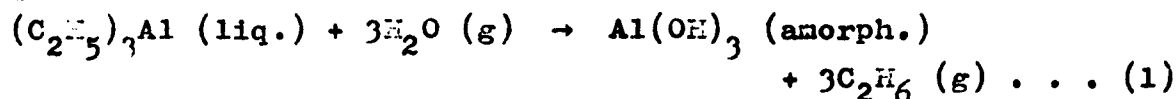


TABLE 1

Heat of hydrolysis of triethyl aluminium

Wt. water (gr.)	$-\Delta H$ (kcal./mole of $\text{Et}_3\text{Al}$ )	
0.0106	155.9	
0.0116	151.1	
0.0212	162.2	
0.0206	150.0	
0.0240	157.8	
0.0192	152.0	<u>Mean <math>\Delta H = -154.8 \pm 2.0</math></u> <u>kcal./mole</u>

DISCUSSION

The heat of formation of triethylaluminium can be calculated from the thermochemical relation

$$\Delta H \text{ (hydrolysis)} = \Delta H_f^\circ[\text{Al(OH)}_3, \text{ amorph.}] + 3\Delta H_f^\circ(\text{C}_2\text{H}_6, \text{ g}) - \Delta H_f^\circ[(\text{C}_2\text{H}_5)_3\text{Al, liq.}] - 3\Delta H_f^\circ(\text{H}_2\text{O, g}).$$

The following heats of formation are used:  $\text{H}_2\text{O (g)}$ ,  $-57.80$  and  $\text{C}_2\text{H}_6 \text{ (g)}$ ,  $-20.24^2$  and  $\text{Al(OH)}_3 \text{ (amorph.)}$ ,  $304 \pm 4$  kcal./mole.<sup>2, 3</sup> These lead to the value

$$\underline{\Delta H_f^\circ[(\text{C}_2\text{H}_5)_3\text{Al, liq.}] = -36.5 \pm 5.5 \text{ kcal./mole.}}$$

A large part of the uncertainty attached to this value is due to the limits of error associated with the heat

of formation of amorphous aluminium hydroxide. Also, it may be that under the particular conditions hydrargillite,  $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}-\alpha$  (cryst.) or bayerite,  $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}-\beta$  (cryst.) is produced in the reaction. However, this is of little consequence. Their heats of formation are  $-615.4 \pm 5$ , and  $-612.6 \pm 6$  kcal./mole, or  $-307.7 \pm 2.5$  and  $306.3 \pm 3$  kcal. for one half mole, respectively. These values differ only slightly from the heat of formation of amorphous aluminium hydroxide, and are well within the uncertainty attached to the figure of  $-304 \pm 4$  kcal./mole. In addition, it may be that the aluminium hydroxide formed in this reaction is slightly soluble in the liquid triethylaluminium.

These difficulties might have been overcome by measuring the heat of solution of the precipitated aluminium hydroxide in (a) triethylaluminium and (b) hydrochloric acid solution. It would then have been possible to express the heat of formation of triethylaluminium in terms of the heat of formation of the more well-defined state of an aluminium chloride solution. However, with the particular design of the calorimeter and the presence of unchanged triethylaluminium in the reaction vessel, it was not possible to extract the aluminium hydroxide precipitate.

The mean bond dissociation energy for the aluminium-carbon bond in triethyl aluminium,  $\bar{D}(\text{Al}-\text{C}_2\text{H}_5)$ , can be calculated from the relationship

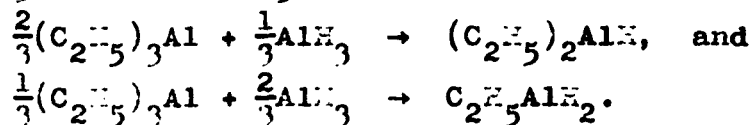
$$\bar{D}(\text{Al}-\text{C}_2\text{H}_5) = \frac{1}{3}\Delta\text{Hf}^\circ(\text{Al}, \text{g}) + \Delta\text{Hf}^\circ(\text{C}_2\text{H}_5, \text{g}) - \frac{1}{3}\Delta\text{Hf}^\circ[(\text{C}_2\text{H}_5)_3\text{Al}, \text{g}].$$

For this calculation to be made it is necessary to derive a value for the heat of formation of gaseous, monomeric triethylaluminium from our value for the liquid compound.

Laubengayer and Gilliam<sup>4</sup> have measured the vapour pressure of liquid triethylaluminium over the range 110 - 140°C and the molecular weight of the vapour over the range 140 - 200°C. The heat of vaporisation at the mean temperature of 125°C is  $16.6 \pm 0.4$  kcal./mole. At 150°C

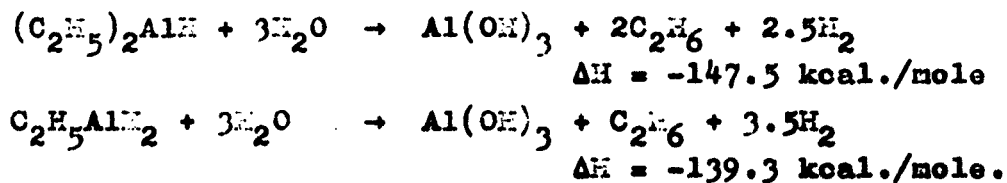
triethylaluminium appears to be about 12% associated to the dimer. For the process  $(C_2H_5)_3Al$  (liq.)  $\rightarrow$   $(C_2H_5)_3Al$  (monomer, g) we estimate the value  $\Delta H = 17.5 \pm 0.5$  kcal./mole. Using our value for the heat of formation of liquid triethylaluminium we derive  $\Delta H_f^\circ[(C_2H_5)_3Al, g] = -19.0 \pm 6.0$  kcal./mole. Incorporating the values  $\Delta H_f^\circ(Al, g)$ , 75.0 kcal./g.atom;<sup>5</sup> and  $\Delta H_f^\circ(C_2H_5, g)$ , 25.5  $\pm$  2 kcal./mole;<sup>6</sup> we obtain the value  $\bar{D}(Al-C_2H_5) = 56.8 \pm 4.0$  kcal./mole.

Taking the values  $\Delta H_f^\circ[(C_2H_5)_3Al, \text{monomer}, g] = -19.0 \pm 6.0$ , and  $\Delta H_f^\circ[AlH_3, \text{monomer}, g] = 13 \pm 10$  kcal./mole,<sup>3</sup> we may estimate the heats of formation of the compounds  $(C_2H_5)_2AlH$  and  $C_2H_5AlH_2$  from the hypothetical reactions:



If we assume that for these gas-phase reactions the  $\Delta H$  values are zero, (i.e. that bond energies are constant from one molecule to another) then we calculate the heats of formation  $\Delta H_f^\circ[(C_2H_5)_2AlH, \text{monomer}, g] = -7 \pm 7$  and  $\Delta H_f^\circ[C_2H_5AlH_2, \text{monomer}, g] = +6 \pm 8$  kcal./mole. It is difficult to estimate accurately the heats of association in the gas phase, and the latent heat of vaporisation. However, using a figure of 17.5 kcal./mole, for the sum of these two quantities (the same as for triethylaluminium) the heats of formation of the liquid compounds will be  $-24.5 \pm 7$  and  $-11.5 \pm 8$  kcal./mole, respectively.

Using these, and other heats of formation quoted previously, the heats of the following hydrolysis reactions may be calculated.



A 2.9% impurity of diethylaluminium hydride and ethylaluminium dihydride in triethylaluminium (for which we have a heat of hydrolysis of  $\Delta H = -154.8 \pm 2.0$  kcal./mole) would probably introduce an error of not more than 0.5 kcal./mole in the heat of hydrolysis. Likewise the error introduced by 0.8% aluminium ethoxide and 0.9% tributylaluminium will be small. These errors are well within our experimental uncertainty of  $\pm 2.0$  kcal./mole and are, therefore, neglected.

#### References

1. Fedley, Chernick & Skinner, Trans. Faraday Soc., 1957, 53, 1612.
2. National Bureau of Standards Circular 500, Washington D.C., 1952.
3. National Bureau of Standards Report 6484, Washington D.C., 1959
4. Laubengayer & Gilliam, J. Amer. Chem Soc., 1941, 63, 477.
5. Cottrell, "The Strengths of Chemical Bonds", Butterworths, 2nd. edn., 1958.
6. Skinner, "The Royal Institute of Chemistry Monograph No. 3", London, 1958.

Trimethylaluminium

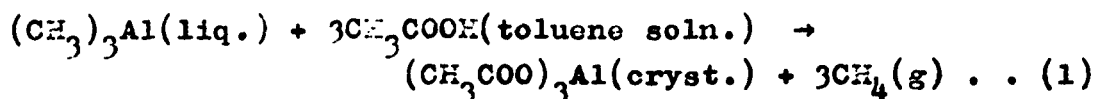
By C.T. Mortimer and P.W. Sellers.

The heat of reaction between liquid trimethylaluminium and acetic acid in toluene solution to give aluminium triacetate and methane has been measured. The heat of reaction between aluminium triacetate and aqueous 4.36*M*-hydrochloric acid has been measured. These data have been used to calculate the heats of formation of liquid trimethylaluminium,  $\Delta H_f^\circ = -36.1 \pm 1.6$  kcal./mole and crystalline aluminium triacetate,  $\Delta H_f^\circ = -451.8 \pm 0.8$  kcal./mole. The mean bond dissociation energy  $\bar{D}(\text{Al-H}) = 64.5 \pm 2.0$  kcal./mole is calculated.

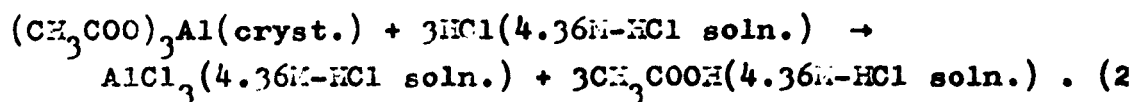
Accurate determination of the heats of formation of trialkylaluminium compounds is difficult because of their high reactivity. There are few reactions of these compounds which are stoichiometrically well-defined and which are also suitable for thermochemical study. Long and Norrish<sup>1</sup> measured the heat of combustion of trimethylaluminium using a static-bomb calorimeter. However, degradative oxidation under these conditions is not well defined. The difficulties which are encountered in determining the heats of combustion of organo-metallic compounds have been reviewed by Good and Scott.<sup>2</sup> It seemed likely that measurement of the heat of a reaction which was less violent and more well-defined than degradative oxidation might provide a more precise value for the heat of formation of trimethylaluminium.

According to Whincup,<sup>3</sup> a 30% solution of glacial acetic acid in toluene, at  $-50^\circ$ , provides a reagent for

the liberation of the methyl groups of trimethylaluminium as methane, with little tendency to form unsaturated hydrocarbons. The low temperature of  $-50^{\circ}$  was unsuitable for our thermochemical study, and the reaction was carried out at  $25^{\circ}$ . The heat of this reaction,  $\Delta H_1$ , has been measured, using a rotating-bomb calorimeter:



The heat of formation of aluminium triacetate was not available, and to provide data from which it might be calculated, the heat of solution of this compound in 4.36N-hydrochloric acid was measured:



A Dewar-vessel calorimeter was used to measure the heat of this reaction.

### EXPERIMENTAL

Compounds.- Trimethylaluminium was supplied in steel containers by the Carrington Research laboratory of Petrochemicals Ltd. It had been analysed by gasimetric methods,<sup>4</sup> based on the liberation of the alkyl groups as methane, developed in that Laboratory. The trimethylaluminium was 99.5% pure. It was found difficult to purify further by fractional distillation. Aluminium triacetate was prepared<sup>5</sup> from aluminium chloride and acetic acid. It was analysed for aluminium colorimetrically as oxinate. Found: Al, 13.69%; calc. 13.21%.

Units.- Heat quantities are given in units of the thermochemical calorie, 1 cal. = 4.1840 abs. J.

Rotating-bomb Calorimetry.— The reaction between trimethylaluminum and acetic acid was carried out in a rotating-bomb calorimeter, which was designed and constructed by Dr. S. Sunner at the University of Lund, Sweden. The bomb was of stainless steel and was platinum lined. It had a capacity of 261 ml. The bomb was held on two point bearings at its top and bottom in a jaw, which was rotated by means of a synchronous motor. A mitred cog at the centre of this jaw engaged a set of mitred teeth round the middle of the bomb. As the jaw and bomb rotated end over end, this mitred gear provided a rotation about the point bearings supporting the bomb in the jaw.

Temperature measurements were made by measuring the change in resistance,  $\Delta R$ , of a platinum resistance thermometer. The fundamental interval of this thermometer was 9.3047 ohms between  $0^{\circ}$  and  $100^{\circ}$ .

The energy equivalent of the calorimeter,  $E_s$ , was determined according to the method of Frosen,<sup>6</sup> by combustion of a sample of benzoic acid (B.D.E. Thermochemical Standard, batch no. 760161), having  $-\Delta U_b = 6319.1 \pm 0.7$  cal./g, standard deviation,  $\bar{s}B = \pm 0.01\%$ . The bomb was charged with 1 ml. of water and with oxygen at an initial pressure of 30 atm. Each sample was fired at  $25^{\circ}$ . The combustions were initiated by a platinum wire and cotton fuse. The energy equivalent of the uncharged bomb, at  $25^{\circ}$ , was calculated using specific heat data given by Hubbard, Scott and Waddington.<sup>7</sup>  $E_s = 69744.6$  cal./ohm.  $\bar{s}B = \pm 0.03\%$ . The heats evolved in ancillary processes were taken to have the values quoted previously.<sup>8</sup>

Trimethylaluminum was distilled into thin, weighed glass phials which were placed in a platinum crucible in the bomb. The bomb was charged with glacial acetic acid (5 ml.) in dry toluene (13.5 ml.). A small quantity of acetic anhydride (1.5 ml.) was also added to ensure the absence of free water in the solution. The bomb was

flushed out with dry, oxygen-free nitrogen at atmospheric pressure. When the bomb was rotated the glass phial of trimethylaluminium fell out of the crucible, was broken, and reaction occurred. The heat change which accompanied this reaction was measured.

The gaseous reaction products were analysed by gas-phase chromatography. A silica-gol column was used for the separation of methane and hydrogen, and a combination of two columns, of dimethyl sulpholane and of dinonyl phthalate for the higher hydrocarbons. The only gaseous products detected were methane, hydrogen, and a hydrocarbon,  $C_4H_8$ , which was identified as isobutene using a glycol/silver nitrate column. These analyses were carried out by the Carrington Research Laboratory. The amounts of methane, hydrogen and isobutene are shown in Table 1, as % v/v of the total gaseous products of reaction.

The heat correction,  $q(C_4H_8)$ , for the hydrogenation of isobutene to methane, i.e.,  $C_4H_8 + 4H_2 \rightarrow 4CH_4$ , may be calculated from the heats of formation of the gaseous compounds; isobutene, -4.04; and methane, -17.889 kcal./mole.<sup>9</sup> In three experiments there was slightly more hydrogen, and in two experiments less hydrogen than the quantity required for this hydrogenation. The cause of this is uncertain and no heat correction has been made to allow for the excess, or deficiency of hydrogen.

The bomb was opened in a dry-box and the gelatinous solid separated from the toluene solution. An X-ray powder photograph of this compound was identical with that of aluminium triacetate. The compound was quickly hydrolysed to a white, finely divided powder on exposure to the atmosphere. An X-ray powder photograph of this compound was the same as that of aluminium diacetate hydrate,  $Al(OH)(CH_3COO)_2 \cdot H_2O$ . The infra-red absorption spectrum of the white solid showed peaks at 1600 and 3500  $cm^{-1}$ , indicating the presence of acetate

groups and of water of crystallization.<sup>10</sup> A micro-analysis was carried out. Found: C, 26.18; H, 5.03%. Calc. for  $\text{Al}(\text{OH})(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ : C, 26.67; H, 5.00%. On this evidence it was concluded that aluminium triacetate was produced in the bomb reaction.

No trace of carbon was found in the experiments for which results are reported here. Attempts were made to increase the accuracy of the thermochemical measurements by increasing the quantities of trimethylaluminium, acetic acid and toluene. In these experiments large amounts of carbon and unsaturated hydrocarbons were produced.

The heat of solution of methane in toluene solution was measured by breaking phials of 25 ml. of toluene solution into an atmosphere of methane in the bomb. The heat change was negligible. The heat of solution of aluminium triacetate was found to be negligible.

The results of the experiments are shown in Table 1. The decrease in internal energy of the system,  $-\Delta U$ , due to the reaction of one mole of trimethylaluminium in its standard state, at  $25^\circ$ , is given by

$$-\Delta U = 10^{-3} \left[ \frac{1}{\bar{M}} (\bar{E}_g + \bar{E}_c) \Delta R + q(\text{C}_4\text{H}_8) \right]$$

where  $\bar{E}_c$  is the energy equivalent of the contents of the bomb after the reaction, calculated by using the following specific heat values: toluene, 0.404; acetic acid, 0.480; acetic anhydride, 0.434; methane,<sup>11</sup> 0.530; and nitrogen,<sup>12</sup> 0.243 cal./deg./g. at  $25^\circ$ . The standard heat of reaction,  $\Delta H_1$ , is derived using the relation  $-\Delta H_1 = -\Delta U - \Delta nRT$ , where  $\Delta n$  is the number of moles of gas produced in the reaction. The overall uncertainty interval associated with the value of  $\Delta H_1$  is twice the standard deviation,  $2\bar{s}$ .

Devar-vessel Calorimetry.— The heats of solution were measured in calorimeters which have been described elsewhere.<sup>13,14</sup> The heats of solution of aluminium triacetate

Table 1

Heat of reaction of trimethylaluminium N, 72.07

<u>Experiment</u>	1	2	3	4	5
Wt. $\text{Me}_3\text{Al}$ (g)	0.4819	0.5801	0.6609	0.6435	0.6620
$\Delta R$ (ohm)	0.01193	0.01411	0.01590	0.01526	0.0158
$\text{CH}_4$ (%v/v)	98.7	91.9	97.8	97.4	83.5
$\text{C}_4\text{H}_8$ (% v/v)	0.0	1.4	1.9	2.2	2.9
$\text{H}_2$ (% v/v)	1.3	6.7	0.3	0.4	13.6
$q(\text{C}_4\text{H}_8)$ (cal.)	0.0	23.0	33.4	37.8	55.6
$E_c$ (cal./ohm)	115.6	115.4	112.3	112.5	112.3
$-\Delta U$ (kcal./mole)	124.5	125.2	124.6	123.5	126.2

Mean  $-\Delta U = 124.3$  kcal./mole (standard deviation of mean  $\pm 0.44$  kcal./mole).  $\bar{s}\Delta U = \pm 0.35\%$ ;  $\bar{s} = \pm 0.35\%$ ;

$\Delta nRT = 1.79$  kcal./mole.

$-\Delta H_1 = 123.0 \pm 0.9$  kcal./mole.

and acetic acid in hydrochloric acid were measured in a spherical, silvered Dewar vessel (capacity 1 litre) with a long neck. For the solution of acetic acid in toluene, a smaller cylindrical, silvered Dewar vessel (capacity 300 ml.) was used. Both vessels were immersed in a thermostat bath at  $25^\circ$ . Temperature measurements were made from the resistance change of a thermistor element. The calorimeter was calibrated electrically by the substitution method, to an accuracy of  $\pm 0.20\%$ .

Results of the measurement of the heat of solution of aluminium triacetate in 4.36M-hydrochloric acid,  $\Delta H_2$ , to yield the products in solution are shown in Table 2. The heat of solution of acetic acid in 4.36M-hydrochloric acid, to give solutions of the same concentration of acetic acid as those produced when aluminium triacetate was dissolved,

has been measured as  $\Delta H_{\text{soln.}} = -0.12 \pm 0.01$  kcal./mole.

The heat of solution of acetic acid in a solution of acetic anhydride in toluene, to give solutions of the same concentration as those in which the reaction of trimethylaluminium occurred, has been measured as  $\Delta H_{\text{soln.}} = +0.21 \pm 0.04$  kcal./mole. The uncertainties associated with these values of  $\Delta H$  are twice the overall standard deviations.

Table 2

Heat of solution of aluminium triacetate M, 204.10

<u>Experiment</u>	1	2	3	4	5
Wt. $(\text{CH}_3\text{COO})_3\text{Al}(\text{g})$	0.7214	0.4730	0.4301	0.8441	0.9670
$-\Delta H_2$ (kcal./mole)	22.06	23.13	22.97	22.34	22.66

Mean  $-\Delta H_2 = 22.63 \pm 0.42$  kcal./mole.

### DISCUSSION

The heat of formation of crystalline aluminium triacetate can be calculated from the thermochemical relation

$$\Delta H_2 = \Delta H_f^\circ(\text{AlCl}_3, 4.36\text{M-HCl soln.}) - 3\Delta H_f^\circ(\text{HCl}, 4.36\text{M soln.}) + 3\Delta H_f^\circ(\text{CH}_3\text{COOH}, 4.36\text{M-HCl soln.}) - \Delta H_f^\circ[(\text{CH}_3\text{COO})_3\text{Al, cryst.}]$$

Coughlin<sup>15</sup> has measured the difference in heats of formation  $\Delta H_f^\circ(\text{AlCl}_3, 4.36\text{M-HCl soln.}) - 3\Delta H_f^\circ(\text{HCl}, 4.36\text{M soln.}) = -127.05 \pm 0.12$  kcal./mole. The value  $\Delta H_f^\circ(\text{CH}_3\text{COOH}, 4.36\text{M-HCl soln.}) = -115.3 \pm 0.1$  kcal./mole may be calculated from  $\Delta H_f^\circ(\text{CH}_3\text{COOH, liq.}) = -115.7 \pm 0.1$  kcal./mole,<sup>16</sup> and our measured heat of solution  $\Delta H_{\text{soln.}} = -0.12 \pm 0.01$  kcal./mole. Using these heats of formation the value is derived  $\Delta H_f^\circ[(\text{CH}_3\text{COO})_3\text{Al, cryst.}] = -451.3 \pm 0.3$  kcal./mole. This can be used to determine the heat of formation of liquid trimethylaluminium from the

relation  $\Delta H_1 = \Delta H_f^\circ[(\text{CH}_3\text{COO})_3\text{Al, cryst.}] + 3\Delta H_f^\circ(\text{CH}_4, \text{g.}) - 3\Delta H_f^\circ(\text{CH}_3\text{COOH, toluene soln.}) - \Delta H_f^\circ[(\text{CH}_3)_3\text{Al, liq.}]$ . The following heats of formation are then used:  $\text{CH}_4(\text{g.})$ ,<sup>9</sup> -17.889;  $\text{CH}_3\text{COOH}(\text{toluene soln.})$ ,  $-115.5 \pm 0.1$ , calculated from the heat of formation of liquid acetic acid given previously and our measured heat of solution,  $\Delta H_{\text{soln.}} = +0.21 \pm 0.04$  kcal./mole. The heat of formation is then calculated  $\Delta H_f^\circ[(\text{CH}_3)_3\text{Al, liq.}] = -36.1 \pm 1.6$  kcal./mole. This may be compared with a value of  $-28.9 \pm 3.0$  derived from the data given by Long and Horrish.<sup>1</sup>

At  $25^\circ$ , gaseous trimethylaluminium consists of dimeric molecules.<sup>17</sup> The latent heat of vaporisation of liquid trimethylaluminium over the range  $23^\circ - 70^\circ$  was measured by Laubengayer and Gillian<sup>13</sup> as 9.6 kcal./mole of dimer. Recently, McCullough<sup>19</sup> has obtained a more reliable value of  $10.01 \pm 0.05$  kcal./mole of dimer, at  $25^\circ$ . The heat of dissociation of the gaseous dimer to two molecules of monomer has been given<sup>18</sup> as 20.2 kcal./mole of dimer. Hence, for the process  $(\text{CH}_3)_3\text{Al}(\text{liq.}) \rightarrow (\text{CH}_3)_3\text{Al}(\text{g., monomer})$  we have the value  $\Delta H = 15.1$  kcal./mole. Incorporating this with our value for the heat of formation of liquid trimethylaluminium leads to the value  $\Delta H_f^\circ[(\text{CH}_3)_3\text{Al, g., monomer}] = -21.0 \pm 2.0$  kcal./mole.

The mean bond dissociation energy  $\bar{D}(\text{Al-Me})$  for the aluminium-carbon bonds may be derived from the relation  $\bar{D}(\text{Al-Me}) = \Delta H_f^\circ(\text{CH}_3, \text{g.}) + \Delta H_f^\circ(\text{Al, g.}) - \Delta H_f^\circ[(\text{CH}_3)_3\text{Al, g., monomer}]$ . Taking our value for the heat of formation of gaseous trimethylaluminium and the heats of formation:  $\text{CH}_3(\text{g.})$ ,  $32.5 \pm 1$  kcal./mole<sup>20</sup> and  $\text{Al}(\text{g.})$ , 75.0 kcal./g.-atom,<sup>21</sup> we obtain the value  $\bar{D}(\text{Al-Me}) = 64.5 \pm 2.0$  kcal./mole.

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### Illustrations

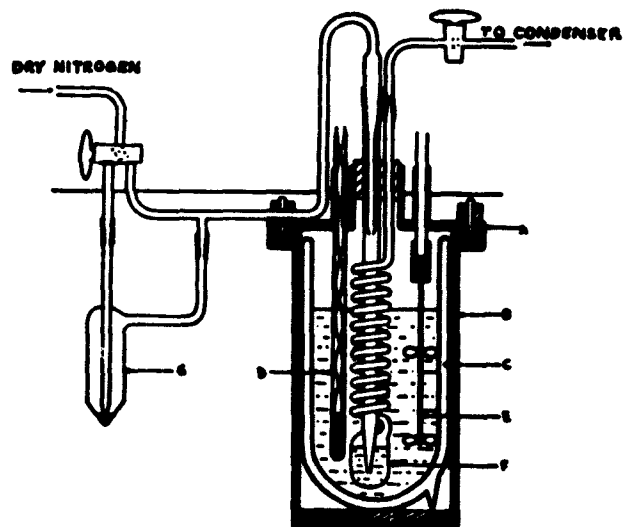
The two calorimeters, which have been used in these investigations, are illustrated on the following pages. The calorimeter used for measuring the heats of hydrolysis of n-butyl-lithium and triethylaluminium is shown in the first diagram. Dry nitrogen enters the reaction vessel, F, either directly, or via the water saturator, G. The reaction vessel is immersed in water contained in a Dewar vessel, C, which fits tightly into a copper can, B. This can is provided with a flanged lid, A. The water is stirred by the propeller, E, and temperature measurements are made by the thermistor element, (not shown) which lies behind the electrical calibration heater, D.

The second illustration shows the rotating-bomb calorimeter, used for the work on trimethylaluminium, "exploded" into its main components. The bomb and rotating mechanism, A, are supported from the lid of a calorimeter can, B, which is filled with water. This water is stirred by the propeller, C. The assembled can hangs inside a metal cavity which is of the same shape, but slightly larger than the can, so that an air gap separates the can and cavity walls. The cavity is submerged in a tank, D, of water which is thermostatted and circulated by a pump, E, round the outside of the cavity and through the lid, F. The calorimeter can is, therefore, surrounded by an isothermal jacket. Temperature changes in the can are measured by the platinum resistance thermometer, not shown in the figure.

The third illustration shows in greater detail the rotating mechanism, supported on a stand for demonstration purposes. The bomb is held on two point bearings at its top and bottom in a jaw, which is rotated by a synchronous motor, G. A nitred cog, H, at the centre of this jaw

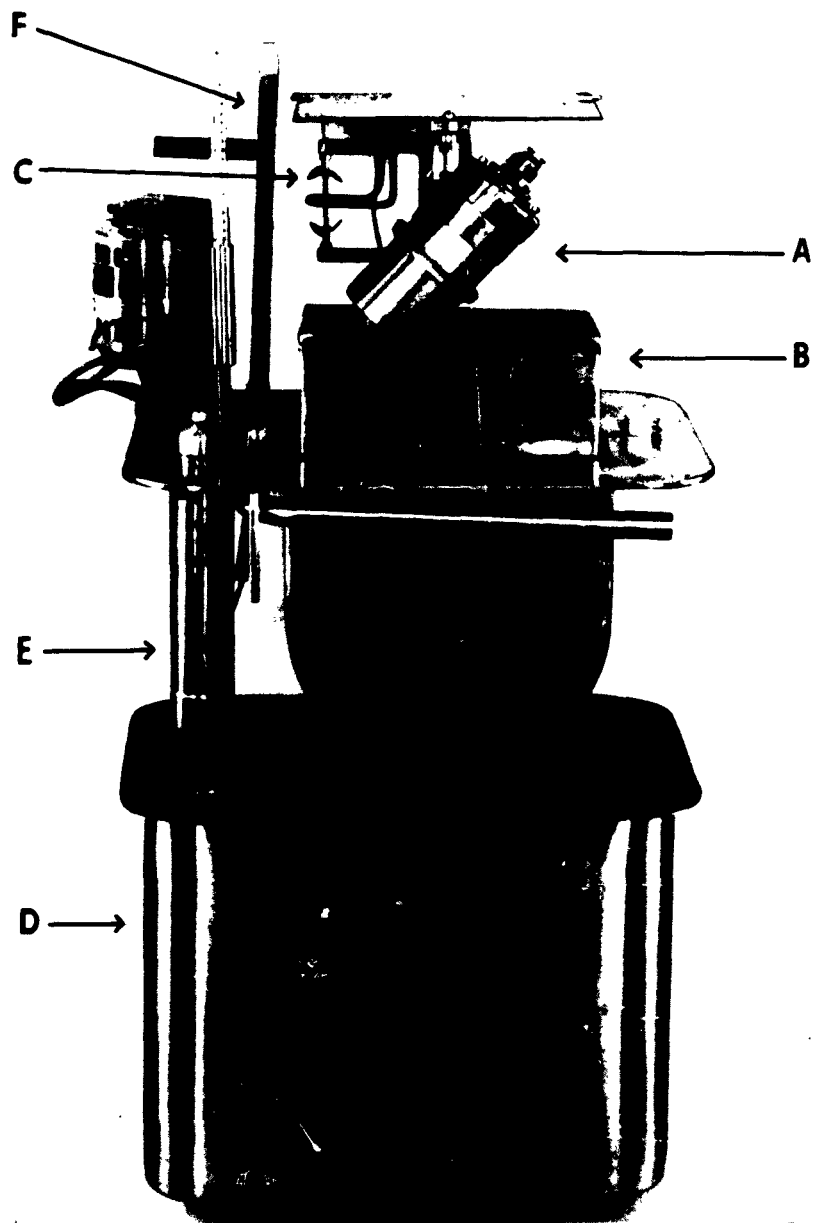
engages a set of mitred teeth round the middle of the bomb. As the jaw and bomb rotate end over end, this mitred gear provides a rotation about the point bearings supporting the bomb in the jaw. Other features shown include the motor, J, which drives the propeller, C, used to stir the water in the calorimeter can; and also the wiring, L, which carries electric current to initiate the combustion.

**CALORIMETER FOR MEASURING HEATS OF HYDROLYSIS  
(WITH WATER VAPOUR, AT 25°C)**



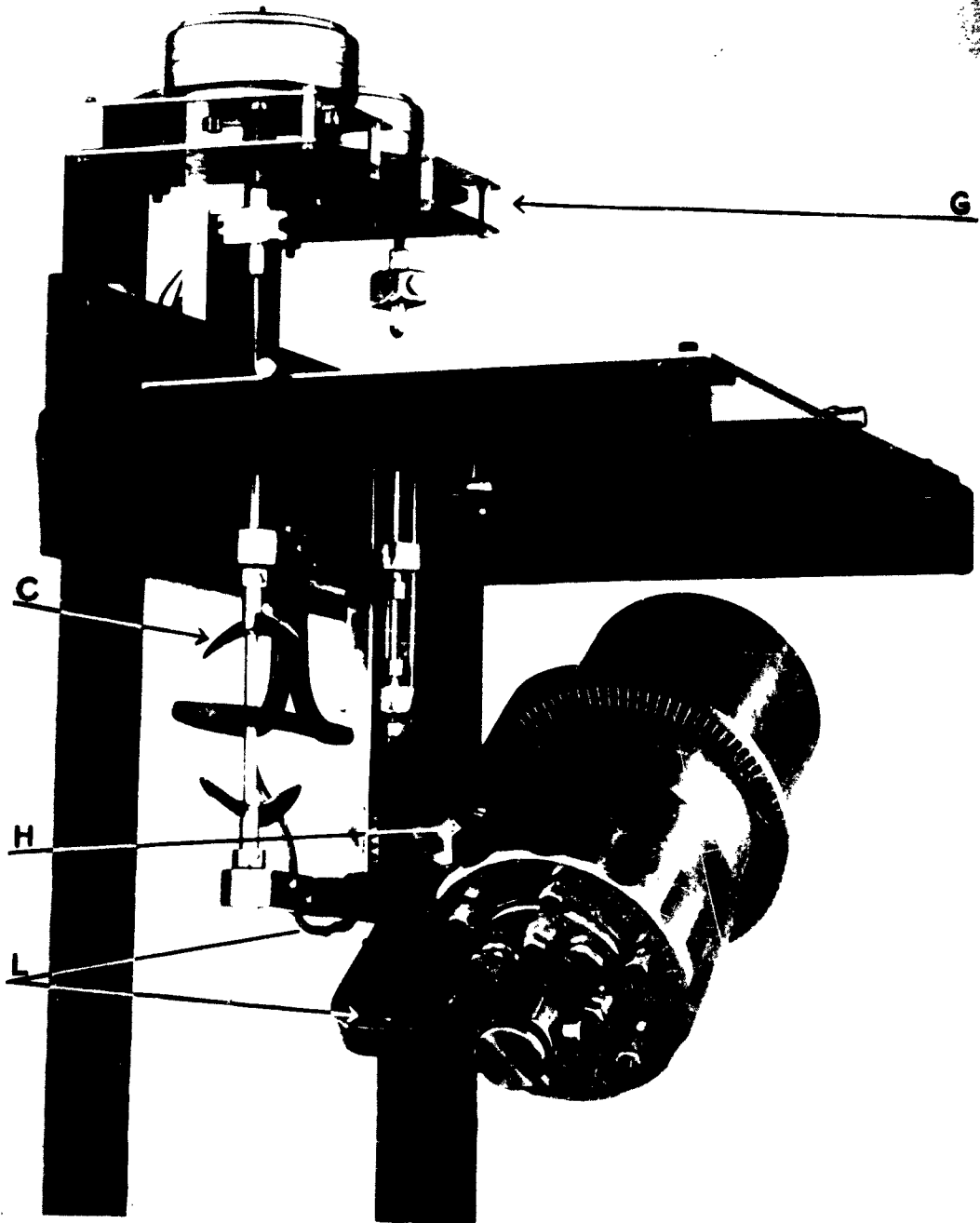
A flange lid; B copper can; C Dewar vessel; D heater;  
E stirrer; F Pyrex reaction vessel; G water container.

**ROTATING-BOMB CALORIMETER FOR MEASURING  
HEATS OF COMBUSTION.**



A bomb held in rotation mechanism; B calorimeter can;  
C propeller stirrer; D tank; E pump; F lid.

ROTATION MECHANISM OF ROTATING-BOMB CALORIMETER  
(SUPPORTED ON A STAND FOR DEMONSTRATION PURPOSES)



C propeller stirrer; G motor driving rotation mechanism;  
H mitred cog; L wiring carrying electrical firing current.

### Conclusions

The major conclusion which may be drawn from this work is that reaction calorimetry, especially in a closed system, is a suitable method for determining the heats of formation of highly reactive organo-metallic compounds.

More particularly, the use of the rotating-bomb calorimeter might be extended to studies of the heats of hydrolysis of such compounds as ethyl-lithium, diethyl-aluminium hydride, or even to the alkyl aluminium halides, such as diethylaluminium chloride or ethylaluminium dichloride.

### Bibliography

The references pertinent to the three investigations are listed as follows:

n-butyl-lithium . . . . .	page 6 (overleaf)
triethylaluminium . . . . .	" 13
trimethylaluminium . . . . .	" 23.

### Symbols

These are defined in the relevant parts of the text.

ASTIA NO.

Contract No. AF 61(052)-307

United States Air Force, Office of Aerospace Research, European Office, Brussels, Belgium. Final Report.

'Heats of Formation and Bond Energies of Organometallic Compounds, n-Butyl-lithium, triethylaluminum and trimethylaluminum', by Colin T. Mortimer.

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