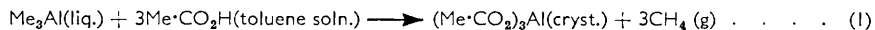**368.** *Heats of Formation and Bond Energies. Part IX.**
Trimethylaluminium and Aluminium Triacetate.

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

The heat of reaction of liquid trimethylaluminium with acetic acid in toluene solution to give aluminium triacetate and methane has been measured. The heat of reaction of aluminium triacetate with aqueous 4·36M-hydrochloric acid has been measured. These data have been used to calculate the heats of formation of liquid trimethylaluminium, $\Delta H_f^\circ = -36\cdot1 \pm 1\cdot6$ kcal./mole, and crystalline aluminium triacetate, $\Delta H_f^\circ = -451\cdot8 \pm 0\cdot8$ kcal./mole The mean bond-dissociation energy, $\bar{D}(\text{Al–Me}) = 64\cdot5 \pm 2\cdot0$ 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 well defined stoicheiometrically and which are also suitable for thermochemical study. Long and Norrish [1] measured the heat of combustion of trimethylaluminium by use of 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 organometallic compounds have been reviewed by Good and Scott.[2] It seemed that measurement of the heat of a reaction which was less violent and better defined than degradative oxidation might provide a more precise value for the heat of formation of trimethylaluminium.

According to Whincup,[3] a 30% solution of glacial acetic acid in toluene, at −50°, provides a reagent for the liberation of the methyl groups of trimethylaluminium as methane, with little tendency to form unsaturated hydrocarbons. This low temperature was unsuitable for our thermochemical study, and the reaction was carried out at 25°. The heat of this reaction (1), ΔH_1, has been measured by use of a rotating-bomb calorimeter. The heat of formation of aluminium triacetate was not available, and to

$$\text{Me}_3\text{Al(liq.)} + 3\text{Me·CO}_2\text{H(toluene soln.)} \longrightarrow (\text{Me·CO}_2)_3\text{Al(cryst.)} + 3\text{CH}_4 \text{ (g)} \quad . \quad . \quad . \quad . \quad (1)$$

provide data from which it might be calculated, the heat of solution of this compound in 4·36M-hydrochloric acid was measured, by use of a Dewar-vessel calorimeter.

$$(\text{Me·CO}_2)_3\text{Al(cryst.)} + 3\text{HCl(4·36M-HCl soln.)} \longrightarrow \text{AlCl}_3(\text{4·36M-HCl soln.}) + 3\text{Me·CO}_2\text{H(4·36M-HCl soln.)} \quad (2)$$

EXPERIMENTAL

Compounds.—Trimethylaluminium was supplied in steel containers by the Carrington Research Laboratory of Petrochemicals Ltd. It had been analysed by gasometric methods,[4] based on the liberation of the alkyl groups as methane, developed in that Laboratory. The trimethylaluminium was 99·5% pure, and was difficult to purify further by fractional distillation. Aluminium triacetate was prepared [5] from aluminium chloride and acetic acid. It was analysed for aluminium colorimetrically as oxinate (Found: Al, 13·7%. Calc. 13·2%).

Units.—Heat quantities are given in units of the thermochemical calorie, 1 cal. = 4·1840 abs. J.

Rotating-bomb Calorimetry.—The reaction between trimethylaluminium and acetic acid was

* Part VIII, *J.*, 1962, 3212.

[1] Long and Norrish, *Phil. Trans.*, 1949, *A*, **241**, 587.

[2] Good and Scott, " Experimental Thermochemistry," vol. 2, ed. Skinner, Interscience, New York, 1962, Chap. 4.

[3] Whincup, Petrochemicals Ltd., Carrington Research Laboratory, Urmston, personal communication.

[4] Ziegler, *Chem. Ber.*, 1955, **88**, 742; *Annalen*, 1954, **589**, 91.

[5] Hood and Ihde, *J. Amer. Chem. Soc.*, 1950, **72**, 2094.

carried out in a calorimeter designed and constructed by Dr. S. Sunner at the University of Lund, Sweden. The bomb had a capacity of 261 ml.

Temperature was measured from the change in resistance, ΔR, of a platinum resistance thermometer, the fundamental interval of which was 9·8047 ohms between 0° and 100°.

The energy equivalent of the calorimeter, E_s, was determined according to the method of Prosen,[6] by combustion of a sample of benzoic acid (B.D.H. Thermochemical Standard, batch no. 760161), having $-\Delta U_b = 6319\cdot1 \pm 0\cdot7$ cal./g. standard deviation, $\bar{s}B = \pm0\cdot01\%$. The energy equivalent of the *uncharged* bomb, at 25°, was calculated by using specific heat data given by Hubbard, Scott, and Waddington.[7] $E_s = 69744\cdot6$ cal./ohm. $\bar{s}E = \pm0\cdot03\%$. The heats evolved in ancillary processes were taken to have the values quoted previously.[8]

Trimethylaluminium 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 (18·5 ml.). A small quantity of acetic anhydride (1·5 ml.) was also added to remove free water from the solution. The bomb was flushed out with dry, oxygen-free nitrogen at atmospheric pressure. When the bomb was rotated the 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-gel column was used for the separation of methane and hydrogen, and a combination of two columns, of dimethyl sulpholan and of dinonyl phthalate, for the higher hydrocarbons. The only gaseous products detected were methane, hydrogen, and isobutene which was identified by using a glycol–silver nitrate column. These analyses were carried out by the Carrington Research Laboratory, and 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.*, $C_4H_8 + 4H_2 \longrightarrow 4CH_4$, can be calculated from the heats of formation of the gaseous compounds: isobutene, $-4\cdot04$; and methane, $-17\cdot889$ kcal./mole.[9] In three experiments there was slightly

TABLE 1.

Heat of reaction of trimethylaluminium (M, 72·07).

Experiment	1	2	3	4	5
Wt. of Me$_3$Al (g.)	0·4819	0·5801	0·6609	0·6435	0·6620
ΔR (ohm)	0·01193	0·01411	0·01590	0·01526	0·01581
CH$_4$ (% v/v)	98·7	91·9	97·8	97·4	83·5
C$_4$H$_8$ (% v/v)	0·0	1·4	1·9	2·2	2·9
H$_2$ (% v/v)	1·3	6·7	0·3	0·4	13·6
$q(C_4H_8)$ (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 $-\Delta U = 124\cdot8$ kcal./mole (standard deviation of mean $\pm0\cdot44$ kcal./mole). $\bar{s}\Delta U = \pm0\cdot35\%$; $\bar{s} = \pm0\cdot35\%$; $\Delta nRT = 1\cdot79$ kcal./mole. $-\Delta H_1 = 123\cdot0 \pm 0\cdot9$ kcal./mole.

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 finely divided white 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)(Me·CO$_2$)$_2$,H$_2$O. The infrared spectrum of the white solid showed peaks at 1600 and 3500 cm.$^{-1}$, indicating the presence of acetate groups and of water of crystallisation.[10] A microanalysis was carried out [Found: C, 26·2; H, 5·05. Calc.

[6] Prosen, " Experimental Thermochemistry," vol. 1, ed. Rossini, Interscience, New York, 1956, Chap. 6.

[7] Hubbard, Scott, and Waddington, ref. 6, Chap. 5.

[8] Bedford, Edmonson, and Mortimer, *J.*, 1962, 2927.

[9] American Petroleum Institute Research Project 44, Carnegie Press, Pittsburg, Pa., 1953.

[10] Cross, " Introduction to Practical Infra-red Spectroscopy," Butterworths, London, 1960.

for Al(OH)(Me·CO$_2$)$_2$,H$_2$O: C, 26·65; 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 thermal 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 toluene solution (25 ml.) into an atmosphere of methane in the bomb. The heat change was negligible. The heat of solution of aluminium triacetate was negligible.

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

$$-\Delta U = 10^{-3}[M(E_s + E_c)\Delta R/m + q(C_4H_8)]$$

where 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; [11] acetic acid, 0·480; [11] acetic anhydride, 0·434; [11] methane, 0·530; [11] and nitrogen, 0·243 cal./deg./g. at 25°.[12] The standard heat of reaction, ΔH_1, is derived from the relation $-\Delta H_1 = -\Delta U - \Delta n\mathbf{R}T$, where Δn is the number of moles of gas produced in the reaction. The overall uncertainty interval associated with the value of ΔH_1 is twice the standard deviation, $2\bar{s}$.

Dewar-vessel Calorimetry.—The heats of solution were measured in calorimeters which have been described elsewhere.[13,14] The heats of solution of aluminium triacetate and acetic acid in hydrochloric acid were measured in a spherical, silvered Dewar vessel (capacity 1 l.) 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°. Temperature measurements were made from the change in resistance of a thermistor element. The calorimeter was calibrated electrically by the substitution method, to an accuracy of ±0·20%.

Results of the measurement of the heat of solution of aluminium triacetate in 4·36M-hydrochloric acid, ΔH_2, to yield the products in solution are shown in Table 2. The heat of solution of

TABLE 2.

Heat of solution of aluminium triacetate (M, 204·10).

Experiment	1	2	3	5	5
Wt. of (Me·CO$_2$)$_3$Al (g.)	0·7214	0·4780	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.

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 ΔH are twice the overall standard deviations.

DISCUSSION

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

$$\Delta H_2 = \Delta H_f°(\text{AlCl}_3, 4·36\text{M-HCl soln.}) - 3\Delta H_f°(\text{HCl}, 4·36\text{M-soln.})$$
$$+ 3\Delta H_f°(\text{Me·CO}_2\text{H}, 4·36\text{M-HCl soln.}) - \Delta H_f°[(\text{Me·CO}_2)_3\text{Al, cryst.}].$$

[11] Heilbron and Bunbury, " Dictionary of Organic Compounds," Eyre and Spottiswoode, London, 1946.
[12] " International Critical Tables," McGraw-Hill, New York, 1926.
[13] Pedley, Skinner, and Chernick, *Trans. Faraday Soc.*, 1957, **53**, 1612.
[14] Fowell and Mortimer, *J.*, 1959, 2913.

Coughlin [15] has measured the *difference* in heats of formation $\Delta H_f^\circ(AlCl_3, 4\cdot36\text{M-HCl soln.}) - 3\Delta H_f^\circ(HCl, 4\cdot36\text{M-soln.}) = -127\cdot05 \pm 0\cdot12$ kcal./mole. The value $\Delta H_f^\circ(Me\cdot CO_2H, 4\cdot36\text{M-HCl soln.}) = -115\cdot8 \pm 0\cdot1$ kcal./mole can be calculated from $\Delta H_f^\circ(Me\cdot CO_2H, liq.) = -115\cdot7 \pm 0\cdot1$ kcal./mole,[16] and our measured heat of solution $\Delta H_{soln.} = -0\cdot12 \pm 0\cdot01$ kcal./mole. From these heats of formation the value is derived $\Delta H_f^\circ[(MeCO_2)_3Al, cryst] = -451\cdot8 \pm 0\cdot8$ kcal./mole. This can be used to determine the heat of formation of liquid trimethylaluminium from the relation

$$\Delta H_1 = \Delta H_f^\circ[(Me\cdot CO_2)_3Al, cryst.] + 3\Delta H_f^\circ(CH_4, g) \\ - 3\Delta H_f^\circ(Me\cdot CO_2H, \text{toluene soln.}) - \Delta H_f^\circ[Me_3Al, liq.].$$

The following heats of formation are then used: CH_4 (g), $-17\cdot889$;[9] $Me\cdot CO_2H$(toluene soln.), $-115\cdot5 \pm 0\cdot1$, calculated from the heat of formation of liquid acetic acid given previously and our measured heat of solution, $\Delta H_{soln.} = +0\cdot21 \pm 0\cdot04$ kcal./mole. The heat of formation is then calculated $\Delta H_f^\circ[Me_3Al, liq.] = -36\cdot1 \pm 1\cdot6$ kcal./mole. This can be compared with a value of $-28\cdot9 \pm 3\cdot0$ derived from the data given by Long and Norrish.[1]

At 25°, gaseous trimethylaluminium consists of dimeric molecules.[17] The latent heat of vaporisation of liquid trimethylaluminium over the range 23—70° was measured by Laubengayer and Gilliam [18] as $9\cdot6$ kcal./mole of dimer. Recently, McCullough [19] has obtained a more reliable value of $10\cdot01 \pm 0\cdot05$ kcal./mole of dimer, at 25°. The heat of dissociation of the gaseous dimer to two molecules of monomer has been given [18] as $20\cdot2$ kcal./mole of dimer. Hence, for the process $Me_3Al(liq.) \longrightarrow Me_3Al(g, \text{monomer})$ we have the value $\Delta H = 15\cdot1$ kcal./mole. Incorporation of this with our value for the heat of formation of liquid trimethylaluminium leads to the value $\Delta H_f^\circ[Me_3Al, g, \text{monomer}] = -21\cdot0 \pm 2\cdot0$ kcal./mole.

The *mean* bond dissociation energy $\bar{D}(Al-Me)$ for the aluminium–carbon bonds can be derived from the relation $\bar{D}(Al-Me) = \Delta H_f^\circ(Me, g) + \Delta H_f^\circ(Al, g) - \Delta H_f^\circ[Me_3Al, g, \text{monomer}]$. Taking our value for the heat of formation of gaseous trimethylaluminium and the heats of formation: $Me(g)$, $32\cdot5 \pm 1$ kcal./mole [20] and $Al(g)$, $75\cdot0$ kcal./g.-atom,[21] we obtain the value $\bar{D}(Al-Me) = 64\cdot5 \pm 2\cdot0$ kcal./mole.

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[15] Coughlin, *J. Amer. Chem. Soc.*, 1956, **78**, 5479.
[16] Evans and Skinner, *Trans. Faraday Soc.*, 1959, **55**, 260.
[17] Pitzer and Gutowsky, *J. Amer. Chem. Soc.*, 1946, **68**, 2204.
[18] Laubengayer and Gilliam, *J. Amer. Chem. Soc.*, 1941, **63**, 477.
[19] McCullough, U.S. Bureau of Mines, Bartlesville, Oklahoma, U.S.A., personal communication.
[20] Skinner, " Modern Aspects of Thermochemistry," *Roy. Inst. Chem.*, Monograph No. 3, 1958.
[21] Cottrell, " The Strengths of Chemical Bonds," 2nd edn., Butterworths, London, 1958.