Thermochemistry of Tri(tropolonato)- and Tri(4-methyltropolonato)-aluminium(III)

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Enthalpies of formation of tri(tropolonato)- and tri(4-methyltropolonato)-aluminium(III) have been determined at 298·15 K by solution calorimetry. The gas-phase enthalpies of formation have been calculated and from these the Al–O bond energies have been derived.

TROPOLONE and 4-methyltropolone† form complexes with metals analogous to pentane-2,4-dionates.[1] The aluminium complexes, [AlL_3] (L = bidentate tropolonate), are crystalline solids, non-ionic, and volatile enough to sublime under reduced pressure. Stability-constant studies[2] and the general behaviour of the tropolonates suggest that they are more stable than the corresponding pentane-2,4-dionates. Like the latter, but rather more reluctantly, they decompose into Al^{3+} and the protonated ligand in the presence of acid. In this paper we make use of this reaction to determine the heats of formation of the complexes tri(tropolonato)- and tri (4-methyltropolonato)-aluminium(III) and the corresponding Al–O bond energies.

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† Tropolone (Htrop) = 2-hydroxycyclohepta-2,4,6-trien-1-one.

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EXPERIMENTAL

The Solution Calorimeter.—The LKB 8700 reaction and solution precision calorimeter was used for all solution reactions. This particular calorimeter has an 18 carat gold stirrer plated with pure gold, which was not attacked by 60% perchloric acid, and a calibrating resistance (R_h) of 50·183 Ω measured at the leads midway between the calorimeter and its jacket; thermistor resistance at 25 °C is 2 000 Ω.

The molar enthalpy of reaction was calculated from the relation $\Delta H = \varepsilon \Delta R_r / n R_{mr}$, where $\Delta R_r = R_i - R_f$, $R_{mr} = (R_i + R_f)/2$, n = number of moles of reactant, and R_i and R_f are the initial and final thermistor resistances in ohms as determined by the Dickinson treatment.[3] The energy constant, ε, of the calorimetric system is given by $\varepsilon = Q_c R_{mc}/\Delta R_c$, where Q_c is an accurately defined quantity of heat supplied electrically *via* the built-in heater, $Q_c = R_h I^2 t / 41\ 840$ cal (R_h is the resistance of the calibrating heater in ohms, I the calibration current in amps, and t the heating time in seconds), and R_{mc} and ΔR_c have the same significance in a calibration experiment as R_{mr} and ΔR_r have in a reaction. The ratio $\Delta R_r : R_{mr}$ is directly proportional to the temperature change.

Thermochemical functions are expressed in terms of ' the thermochemical calorie ' (1 thermochemical calorie = 4·184 J) and refer to the isothermal process at 298·15 K and the true mass, calculated using the atomic weights of 1966 based on the isotope ^{12}C. The uncertainty interval is twice the standard deviation of the mean. A check on the accuracy of the calorimeter was carried out by determining the heat of dissolution of tris[(hydroxymethyl)amino]methane (tham) in dilute hydrochloric acid. The result, −7·118 ± 0·006 kcal mol^{-1}, is in agreement with other workers [4] (−7·120 ± 0·007 kcal mol^{-1}).

Materials.—Aluminium(III) chloride hexahydrate (AnalaR) was purified [5] and analysed for aluminium (Found: Al, 11·2. Calc. for $AlCl_3 \cdot 6OH_2$: Al, 11·2%). ' Constant boiling ' hydrochloric acid was prepared from HCl (AnalaR) by dilution with distilled water. The concentration of the HCl solution was determined by acid–base analyses against $Na_2B_4O_7 \cdot 10OH_2$ after convenient dilution and found to be 4·37M ($HCl \cdot 11 \cdot 6OH_2$). Perchloric acid (AnalaR, 71%) was diluted to *ca.* 60% with water and analysed against $Na_2B_4O_7 \cdot 10OH_2$. The two batches were 9·54 ($HClO_4 \cdot 3 \cdot 5OH_2$) and 9·21M ($HClO_4 \cdot 3 \cdot 7OH_2$) respectively. Tropolone was prepared by a modification of the method of Stevens *et al.*,[6] recrystallised from light petroleum (40—60 °C), sublimed, and recrystallised again from light petroleum, m.p. 51—52 °C (lit., 50—51 °C) (Found: C, 68·7; H, 4·95. Calc. for $C_7H_6O_2$: C, 68·8; H, 4·95%). 4-Methyltropolone was prepared by the method of Haworth and Hobson,[7] sublimed, recrystallised from light petroleum (60—80 °C), and resublimed, m.p. 76 °C (lit., 76—77 [7] and 76 °C [8]) (Found: C, 70·6; H, 5·9. Calc. for $C_8H_8O_2$: C, 70·6; H, 5·9%).

Tri(tropolonato)aluminium(III), [Al(trop)$_3$].—A solution of aluminium(III) potassium sulphate dodecahydrate (AnalaR, 3·2 g) in water (30 cm^3) was slowly added to a solution of tropolone (2·5 g) in ethanol (100 cm^3). The solution was boiled until precipitation began and then allowed to cool. The solid was filtered, washed well with water, dried, and recrystallised twice from benzene–light petroleum (80—100 °C), m.p. 350 °C (no decomposition was apparent at this temperature) (Found: C, 64·4; H, 3·95; Al, 6·90. Calc. for $C_{21}H_{15}AlO_6$: C, 64·4; H, 3·85; Al, 6·90%).

Tri(4-methyltropolonato)aluminium(III), [Al(4-Metrop)$_3$].—This complex was prepared in the same way as [Al(trop)$_3$]. The complex was washed well with water, dried, and recrystallised twice from benzene, m.p. 316—318 °C (some decomposition took place above 300 °C) (Found: C, 66·6; H, 4·85; Al, 6·25. Calc. for $C_{24}H_{21}AlO_6$: C, 66·7; H, 4·90; Al, 6·25%).

Analyses.—All carbon and hydrogen analyses were carried out in the Microanalytical Service, University of Surrey; aluminium was analysed both by ignition to the oxide Al_2O_3 and by a complexometric method with ethylenediaminetetra-acetic acid (H$_4$edta). Decomposition of the complexes into metal ions and free ligands was extremely slow in dilute acid solutions, but satisfactory results could be obtained using 60% $HClO_4$ as solvent.

RESULTS AND DISCUSSION

The standard enthalpy of formation of the aluminium complexes can be determined from known standard heats of formation and the enthalpy change for reaction (1).

$$HL\ (c) + AlCl_3 \cdot 6OH_2\ (c) \xrightarrow{\Delta H_R} 3\ HCl \cdot 2OH_2 + [AlL_3]\ (c) \qquad (1)$$

This enthalpy change, ΔH_R, is the difference between the enthalpies of solution of the products and reactants. To the calorimetric solvent (100 cm^3), ampoules of ligand and $AlCl_3 \cdot 6OH_2$ were added consecutively and ΔH_2 and ΔH_3 were measured. To a second portion of the same solvent (100·0 cm^3), were added consecutively ampoules of $HCl \cdot 11 \cdot 6OH_2$ and aluminium complex, and ΔH_4 and ΔH_5 were measured. The general procedure, together with the thermochemical cycle, is given in the Scheme.

The quantities of reactants in a particular series of experiments were determined by the amount of $AlCl_3 \cdot 6OH_2$ in the particular ampoule; strict control of stoicheiometry was maintained throughout each series. When this procedure is used the value calculated for ΔH_R refers to the reaction indicated in the first line of the scheme, provided that solutions (A$_3$) and (B$_2$) are identical and that the value of ΔH_6 is zero. As a check of the validity of this, ampoules of solution (B$_2$) were broken into (A$_3$) in the calorimeter; no detectable heat change occurred. The experimental data are in Tables 1 and 2, leading to the ΔH_R values −13·08 ± 0·15 for [Al(trop)$_3$] and +0·26 ± 0·34 kcal mol^{-1} for [Al(4-Metrop)$_3$].

The value of ΔH_1 was calculated from published data [9] on the heat of dilution of perchloric acid: ΔH_1 = −1·428 ± 0·01 and −1·378 ± 0·01 kcal mol^{-1} for the Htrop and 4-Me-Htrop systems, respectively. The following values were taken from the literature: $\Delta H_f^{\ominus}[AlCl_3 \cdot 6OH_2\ (c)] = -643 \cdot 3$;[9] $\Delta H_f^{\ominus}[HCl \cdot 2OH_2] =$

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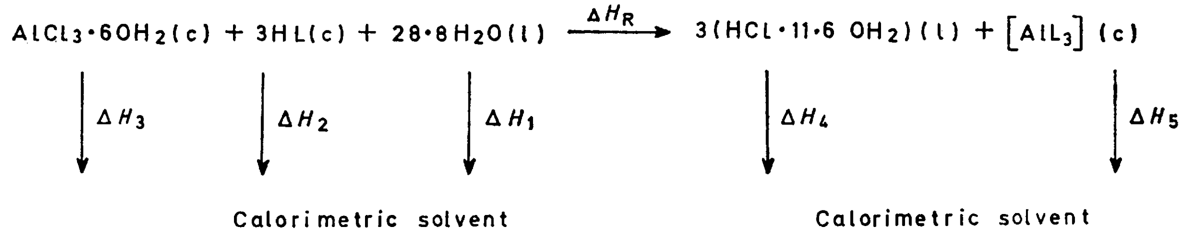

$$\text{Solution }(A_3) \xrightarrow{\Delta H_6\,=\,0} \text{Solution }(B_2)$$

$$\text{Solvent} + H_2O \xrightarrow{\Delta H_1} \text{Solution }(A_1)$$

$$\text{Solution }(A_1) + HL \xrightarrow{\Delta H_2} \text{Solution }(A_2)$$

$$\text{Solution }(A_2) + AlCl_3{\cdot}6\,OH_2 \xrightarrow{\Delta H_3} \text{Solution }(A_3)$$

$$\text{Solvent} + HCl{\cdot}11{\cdot}6\,OH_2 \xrightarrow{\Delta H_4} \text{Solution }(B_1)$$

$$\text{Solution }(B_1) + [AlL_3] \xrightarrow{\Delta H_5} \text{Solution }(B_2)$$

$$\Delta H_R = 28{\cdot}8\,\Delta H_1 + 3\Delta H_2 + \Delta H_3 - 3\Delta H_4 - \Delta H_5 + \Delta H_6$$

TABLE 1

Enthalpy of formation of $[Al(trop)_3]$

(a) Addition of $AlCl_3{\cdot}6OH_2$ to solution (A_2)

$AlCl_3{\cdot}6OH_2$ (10^3 amount/mol)	$10^3(\Delta R/R_m)$	ε	ΔH_3/kcal mol^{-1}
5·0580	2·3811	2 144·4	+10·096
5·1847	2·4402	2 139·0	+10·067
4·9491	2·3283	2 127·9	+10·011
5·1027	2·4254	2 135·4	+10·150
5·1926	2·4233	2 136·9	+10·013
			Mean
			+10·07 ± 0·05

(b) Addition of tropolone to solution (A_1)

Htrop (10^4 amount/mol)	$10^3(\Delta R/R_m)$	ε	ΔH_2/kcal mol^{-1}
15·1771	1·3647	2 124·8	−1·911
15·5595	1·4028	2 079·5	−1·875
14·8537	1·3540	2 141·5	−1·952
15·3040	1·4054	2 126·6	−1·953
15·5710	1·4268	2 117·7	−1·940
			Mean
			−1·93 ± 0·03

(c) Addition of $HCl{\cdot}11{\cdot}6OH_2$ to solvent $HClO_4{\cdot}3{\cdot}71OH_2$

$HCl{\cdot}11{\cdot}6OH_2$ (10^4 amount/mol)	$10^3(\Delta R/R_m)$	ε	ΔH_4/kcal mol^{-1}
15·2078	4·6670	2 130·0	−6·536
15·5360	4·7972	2 143·0	−6·617
14·8116	4·5706	2 140·5	−6·605
15·3016	4·7097	2 148·6	−6·613
15·5474	4·8074	2 146·5	−6·637
			Mean
			−6·60 ± 0·3

(d) Addition of $[Al(trop)_3]$ to solution (B_1)

$[Al(trop)_3]$ (10^4 amount/mol)	$10^4(\Delta R/R_m)$	ε	ΔH_5/kcal mol^{-1}
4·9381	9·1113	2 132·3	−3·934
5·1756	9·5639	2 094·6	−3·870
4·8905	9·1466	2 133·3	−3·990
5·1018	9·5809	2 146·8	−4·031
5·1843	9·7579	2 127·7	−4·005
			Mean
			−3·97 ± 0·06

TABLE 2

Enthalpy of formation of $[Al(4\text{-}Metrop)_3]$

(a) Addition of $AlCl_3{\cdot}6OH_2$ to solution (A_1)

$AlCl_3{\cdot}6OH_2$ (10^4 amount/mol)	$10^3(\Delta R/R_m)$	ε	ΔH_2/kcal mol^{-1}
5·1048	2·7374	2 091·6	+11·206
5·0190	2·6631	2 085·4	+11·065
4·9747	2·6992	2 087·8	+11·328
4·9818	2·6206	2 128·6	+11·197
5·1690	2·7237	2 122·2	+11·183
5·1110	2·7252	2 119·4	+11·301
			Mean
			+11·21 ± 0·08

(b) Addition of 4-methyltropolone to solution (A_2)

4-Me-Htrop (10^4 amount/mol)	$10^3(\Delta R/R_m)$	ε	ΔH_3/kcal mol^{-1}
15·3179	1·1868	2 086·8	−1·617
15·0655	1·3020	2 080·8	−1·798
14·9032	1·1902	2 128·6	−1·700
14·9495	1·1856	2 126·5	−1·686
15·5070	1·2704	2 119·1	−1·736
15·3300	1·2494	2 115·4	−1·724
			Mean
			−1·71 ± 0·05

(c) Addition of $HCl{\cdot}11{\cdot}6OH_2$ to solvent $HClO_4{\cdot}3{\cdot}5OH_2$

$HCl{\cdot}11{\cdot}6OH_2$ (10^4 amount/mol)	$10^3(\Delta R/R_m)$	ε	ΔH_4/kcal mol^{-1}
15·1829	5·8334	2 132·7	−8·194
15·0631	5·9405	2 085·4	−8·224
14·9245	5·8538	2 083·0	−8·170
14·9596	5·8607	2 134·8	−8·363
15·5062	5·8551	2 126·9	−8·059
15·3758	5·8239	2 133·9	−8·083
			Mean
			−8·19 ± 0·09

(d) Addition of $[Al(4\text{-}Metrop)_3]$ to solution (B_1)

$[Al(4\text{-}Metrop)_3]$ (10^4 amount/mol)	$10^3(\Delta R/R_m)$	ε	ΔH_5/kcal mol^{-1}
5·1102	2·2342	2 115·2	−9·248
5·1062	2·2079	2 108·8	−9·118
5·0029	2·1268	2 163·1	−9·196
5·0188	2·2580	2 082·2	−9·480
5·3650	2·3824	2 127·3	−9·446
5·1305	2·2331	2 137·1	−9·302
			Mean
			−9·30 ± 0·11

$-170{\cdot}3$;[9] $\Delta H_f^\ominus$[Hpd (g)]* $= -92{\cdot}3 \pm 0{\cdot}4$;[5,10] $\Delta H_f^\ominus$[Htrop (g)] $= -37{\cdot}1 \pm 0{\cdot}2$;[10] and $\Delta H_f^\ominus$ [4-Me-Htrop (g)] $= -44{\cdot}9 \pm 0{\cdot}5$ kcal mol^{-1} (estimated by the Laidler method[10]). Standard enthalpies of formation of the solid complexes are in Table 3 together with their enthalpies of sublimation and of formation in the gaseous state.

TABLE 3

Complex	$\Delta H_f^\ominus$ (c)	$\Delta H_{subl}^\ominus$	$\Delta H_f^\ominus$ (g)
[Al(pd)$_3$]	$-428{\cdot}46 \pm 0{\cdot}67$ [a]	$29{\cdot}1 \pm 1{\cdot}0$ [b]	$-399{\cdot}4 \pm 1{\cdot}2$
[Al(trop)$_3$]	$-316{\cdot}96 \pm 0{\cdot}66$	$30{\cdot}0 \pm 5{\cdot}0$ [c]	$-287{\cdot}0 \pm 5{\cdot}0$
[Al(4-Metrop)$_3$]	$-329{\cdot}8 \pm 2{\cdot}2$	$30{\cdot}0 \pm 5{\cdot}0$ [c]	$-299{\cdot}8 \pm 5{\cdot}5$

[a] Recalculated from the experimental data in ref. 9, using more accurate literature data. [b] Ref. 11. [c] Estimated.

Enthalpies of sublimation of few co-ordination compounds have been accurately measured, but from a consideration of the existing data it is possible to make a reasonable estimate for the trop and 4-Metrop complexes; the uncertainty must be of the order of 5 kcal mol^{-1}, but this only produces an uncertainty of *ca.* 1 kcal in the bond energy. The metal–oxygen bond strength can be related to the energy needed to break the molecule into metal and ligands, all referred to the gas state [equation (2)] where E(Al–O), the homolytic bond strength, is

$$[\mathrm{AlL_3}]\ (\mathrm{g}) \xrightarrow{\Delta H_f(\mathrm{r})} \mathrm{Al}\ (\mathrm{g}) + 3\ \mathrm{L}^{\bullet}\ (\mathrm{g}) \qquad (2)$$

ΔH_f(r)/6. Calculating the heat of formation of the ligand radical from data for the ligand itself presupposes a knowledge of the dissociation energy of the ligand, that is the heat of reaction of process (3). This is unknown

$$\mathrm{HL}\ (\mathrm{g}) \longrightarrow \mathrm{H}^{\bullet}\ (\mathrm{g}) + \mathrm{L}^{\bullet}\ (\mathrm{g}) \qquad (3)$$

for the tropolones and a reasonable estimate is not easy to make. For Hpd[5] we assumed a value of 100 ± 5 kcal mol^{-1}, but because of the resonating tropolone ring there is reason to suggest that a value closer to phenol (85 kcal mol^{-1}) is more appropriate.[12] Accordingly we take 90 ± 5 kcal mol^{-1} for the dissociation energy of both Htrop and 4-Me-Htrop. The enthalpies of formation of the gaseous-ligand free radicals are 1 ± 5 kcal mol^{-1} for Htrop and -7 ± 5 kcal mol^{-1} for 4-Me-Htrop. As $\Delta H_f^\ominus$[Al (g)] $= 78{\cdot}0$ kcal mol^{-1},[9] values of ΔH_f(r) for the two complexes were calculated and thence the Al–O homolytic bond energies (Table 4).

TABLE 4

Complex	ΔH_f(r)	E(Al–O)	ΔH_f (i)	E'(Al–O)
[Al(pd)$_3$]	347 ± 15	58 ± 3	$1\,478 \pm 15$	246 ± 3
[Al(trop)$_3$]	368 ± 15	61 ± 3	$1\,498 \pm 15$	250 ± 3
[Al(4-Metrop)$_3$]	357 ± 15	60 ± 3	$1\,487 \pm 15$	248 ± 3

It is sometimes convenient to consider the bond energy in terms of the ions as defined by equation (4).

$$[\mathrm{AlL_3}]\ (\mathrm{g}) \xrightarrow{H_f(\mathrm{i})} \mathrm{Al}^{3+}\ (\mathrm{g}) + 3\ \mathrm{L}^{-}\ (\mathrm{g}) \qquad (4)$$

Estimating the electron affinity of the ligands to be approximately equal to that of the oxygen atom, $E_L = 33{\cdot}8$ kcal mol^{-1},[13] enthalpies of formation of the gaseous trop and 4-Metrop ions were calculated to be -33 and -41 kcal mol^{-1} respectively. The heterolytic aluminium–oxygen bond energies, E'(Al–O) $= \Delta H_f$(i)/6, are in Table 4 [$\Delta H_f^\ominus$(Al^{3+}) $= +\,1\,310{\cdot}7$ kcal mol^{-1} (ref. 9)]. The uncertainties in the bond energies are too large to show any differences between the complexes, but it is apparent that the gas-phase bond energies do not give any explanation of the apparently greater stability of metal tropolonates with respect to pentane-2,4-dionates in solution.

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* Hpd = Pentane-2,4-dione.

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