Enthalpies of Solvation of Some Metal Acetylacetonates

By **Roger J. Irving** * and **Ronald A. Schulz,** Department of Chemistry, University of Surrey, Guildford, Surrey

Enthalpies of solution of $M(acac)_3$ (M = Al, Cr, Mn, Fe, and Co) in acetone, benzene, and chloroform have been determined calorimetrically. Specific solvent–solute interaction occurs in the case of chloroform with all solutes and is of the order of 6 kcal (25 kJ) mol^{-1} solute.

INTERACTION between solvent and solid solute has been investigated by a number of techniques, notably i.r.[1-3] and n.m.r. spectroscopy.[4,5] These interactions have an important bearing on solvent effects in the rates of substitution of metal complexes [6] but quantitative data and in particular enthalpies of solvation of non-ionic complexes are remarkably sparse. The tervalent metal acetylacetonates are known to interact with some solvents as evidenced by the solvent-dependence of the chemical shift in their n.m.r. spectra.[7] We now present results for the enthalpies of solution and solvation of several metal acetylacetonates in acetone, benzene, and chloroform, determined by solution calorimetry.

EXPERIMENTAL

Reagents.—Metal acetylacetonates were prepared by standard methods [8] and recrystallised several times from benzene–light petroleum (b.p. 100—120 °C) containing a small quantity of acetylacetone. The crystalline products were heated overnight in a vacuum oven at 50 °C and subsequently stored in the dark over silica gel. Satisfactory analyses for C and H were obtained.

Tris(3-methylacetylacetonato)aluminium(III) was obtained by adding the ligand (0·01 mol) in ethanol (10 ml) to potassium aluminium sulphate (0·002 mol) and sodium acetate (0·06 mol) in water (50 ml). The product was recrystallised several times from benzene–light petroleum containing a small quantity of the ligand and dried as for the acetylacetonates (Found: C, 58·8; H, 7·2. Calc. for $C_{18}H_{27}AlO_6$: C, 59·0; H, 7·4%).

Solvents.—Inconsistent enthalpies of solution were obtained unless the solvents were carefully dried. Benzene and acetone purified by conventional methods could be kept anhydrous by storage over Linde molecular sieve 4A. Chloroform was purified by washing with water and drying (P_2O_5) and, after neutralisation with solid potassium carbonate, distillation under anhydrous conditions. The pure dry solvent was stored in the dark and used within two days of purification.

Calorimetry.—Thermochemical measurements were carried out in a recording solution calorimeter developed from a tested isothermal jacket design [9] having a 100 ml glass reaction vessel. The instrument incorporated a direct-reading temperature-sensing element made up of two chromel–constantan thermocouples connected in parallel. The thermostatically controlled water-bath (±0·001 °C), which provided environmental control for the isothermal jacket, was utilised to stabilise all the temperature-sensitive components of the thermocouple circuit, except the sensing junctions, which were housed in a re-entrant tube on the reaction vessel.

The thermocouple output was applied to a high-gain D.C. amplifier which displayed the equivalent curve of temperature (e.m.f.) against time for the calorimeter on a strip-chart recorder. Sensitivity was increased by using a precision microvolt source in the input circuit, to back off most of the applied signal. Calibration was carried out electrically and reactions where the temperature change was equivalent to an e.m.f. change of *ca.* 1·0 μV were consistently measured to better than ±0·005 μV, *i.e.*, 0·004 cal, a resolution of 1×10^{-4} K.

The sensitivity could be varied over a wide range and even at the lower sensitivities where the operation was considerably simpler there was sufficient reproducibility to obtain significant results.

Procedure.— The parts of the calorimeter were dried before each experiment. The solvent was heated to 27 °C and transferred to the reaction vessel under anhydrous conditions, and the assembled calorimeter allowed to equilibrate in a thermostatted bath at 25 °C. The run was commenced only when a consistent pre-rating slope was obtained. Conditions were so adjusted that the temperature of the reaction vessel always remained below 25 °C. An electrical calibration was carried out immediately after each reaction and the energy change of the chemical reaction was referred to this directly. The heat-transfer characteristics of the calorimeter were reproducible and were checked by the cooling constant *K*.

RESULTS AND DISCUSSION

As the temperature changes in these experiments were quite small, the heat effects due to ampoule breaking and the associated vaporisation of the solvent could not be ignored. A series of experiments was carried out in which empty ampoules were broken in the different solvents giving the following ' heats of ampoule breaking ': benzene; 0·06 ± 0·005 cal, chloroform; 0·11 ± 0·005 cal, and acetone; 0·15 ± 0·008 cal.†

The results for the enthalpies of solution of the metal β-diketonates in the three solvents, corrected for heat of ampoule breaking, are in Table 1. For a particular solvent there are small but significant differences between the different acetylacetonates but these bear no clear relationship to the ionic radii of the metals concerned. For a particular solute the difference in enthalpies of

---

† In this paper, 1 cal = 4·184 J.

[1] M. B. Fairey and R. J. Irving, *Spectrochim. Acta*, 1964, 1757.

[2] L. A. W. Hales and R. J. Irving, *Spectrochim. Acta*, 1967, 2981.

[3] W. Beck and K. Lottes, *Z. Naturforsch.*, 1964, **19**b, 987.

[4] W. G. Schneider, *J. Phys. Chem.*, 1962, **66**, 2653.

[5] H. M. Hutton and T. Schaefer, *Canad. J. Chem.*, 1963, **41**, 187.

[6] R. J. Mawby, F. Basolo, and R. G. Pearson, *J. Amer. Chem. Soc.*, 1964, **86**, 3994.

[7] R. G. Linck and R. E. Sievers, *Inorg. Chem.*, 1966, **5**, 806.

[8] W. C. Fernelius and B. E. Bryant, *Inorg. Synth.*, 1957, **5**, 188.

[9] S. Sunner and I. Wadsö, *Acta Chem. Scand.*, 1959, **13**, 97.

solution are more marked and for each complex the order of solvation is acetone < benzene ≪ chloroform.

The solution process can be regarded as occurring in two steps: (1) conversion of the solid into an ideal gas at the same temperature, *i.e.*, the lattice energy or enthalpy of sublimation of the compound at 25 °C, and (2) dissolution of the discrete solute molecules at 25 °C to give a dilute solution. Ideally one would obtain the enthalpy of solvation by reaction of solute and solvent molecules in the gaseous state at 25 °C. This is not possible and it is assumed that reaction between gaseous solute and liquid solvent provides a reasonable approximation to the enthalpy of solvation.

Enthalpies of sublimation of metal acetylacetonates are difficult to measure so agreement between different investigations is not good. The most recent as well as the most comprehensive set of measurements is that of Melia and Merrifield[10] and we use their values for $Fe(acac)_3$ and $Cr(acac)_3$ in preference to those of earlier workers.

TABLE 1

Molar enthalpies of solution

Solute	Acetone		Benzene		Chloroform	
	w/g[a]	ΔH/kcal	w/g	ΔH/kcal	w/g	ΔH/kcal
$Al(acac)_3$	0·0520	3·64	0·1026	2·90	0·1000	−3·00
	0·1033	3·59	0·0994	2·92	0·1020	−2·97
	0·0963	3·69	0·1016	2·90		
	Mean	3·64	Mean	2·91	Mean	−2·98
$Cr(acac)_3$	0·1003	3·58	0·0998	2·61	0·0986	−2·81
	0·1022	3·54	0·1040	2·60	0·1004	−2·85
					0·0218	−2·88
	Mean	3·56	Mean	2·60	Mean	−2·84
$Mn(acac)_3$	0·1007	3·32	0·1103	2·64	0·1029	−3·06
	0·0997	3·25	0·1007	2·60	0·0995	−3·06
	Mean	3·28	Mean	2·62	Mean	−3·06
$Fe(acac)_3$	0·1010	3·25	0·0999	2·24	0·1028	−2·98
	0·1006	3·32	0·0998	2·23	0·1020	−2·97
	Mean	3·28	Mean	2·24	Mean	−2·98
$Co(acac)_3$	0·1004	3·75	0·0955	2·57	0·0993	−4·07
	0·1005	3·71	0·1000	2·56	0·1006	−4·02
					0·1006	−4·08
	Mean	3·73	Mean	2·56	Mean	−4·05
$Al(Meacac)_3$	0·0954	4·50	0·0825	2·97	0·0838	−3·53

The volume of solvent was 100 ml in all experiments.

[a] w = weight of solute.

From a consideration of the relationships between crystal structure, m.p.s, and enthalpies of sublimation of the metal acetylacetonates[10] we have estimated the following values: $Al(acac)_3$; 25 kcal mol^{-1}, $Co(acac)_3$; 27 kcal mol^{-1}, and $Mn(acac)_3$; 25 kcal mol^{-1}. The estimated value for $Al(acac)_3$ agrees with Frankhauser's[11] experimental value of 25·1 kcal mol^{-1}.

TABLE 2

Enthalpies of solvation, ΔH/kcal

$M(acac)_3(g)$ + solvent (l) ⟶ $M(acac)_3$ (solution 3×10^{-3}M)

	Acetone	Benzene	Chloroform
$Al(acac)_3$	−21·4	−22·1	−28·0
$Cr(acac)_3$	−22·9	−23·9	−29·4
$Mn(acac)_3$	−21·7	−22·4	−28·1
$Fe(acac)_3$	−20·4	−21·5	−26·7
$Co(acac)_3$	−23·3	−24·4	−31·1

Enthalpies of solvation of the gaseous molecules at 25 °C have been calculated and are in Table 2. The uncertainties in the estimation of the heats of sublimation of $Al(acac)_3$ and $Co(acac)_3$ do not permit a valid comparison of the enthalpies of solvation of the metal acetylacetonates in a particular solvent but for a particular metal acetylacetonate a comparison of the solvating effects of the three solvents is valid.

There has been some discussion of solvation effects on metal acetylacetonates by other authors. An n.m.r. spectroscopic study[7] of $Al(acac)_3$ in various solvents suggested that in both acetone and chloroform there was a specific solute–solvent interaction but although the 3-carbon proton on the chelate ring was greatly affected by acetone there was no evidence for its being the site of specific interaction. Further, no distinction could be drawn between hydrogen bonding to the chelating oxygens and direct co-ordination to the metal complex through the relatively open octahedral faces of the complex. Hopkins and Douglas,[12] from a study of distribution constants for metal acetylacetonates between water and organic solvents, suggested that the water molecules interacted with the metal through the octahedral faces of the complex. They found no evidence for hydrogen bonding with chloroform. Fackler *et al.*,[13] however, found intensity changes in the i.r. C–D stretching frequency of deuteriated chloroform characteristic of hydrogen bonding with the compounds $M(acac)_3$ (M = Cr, Mn, Fe, and Co). Steinbach *et al.*[14] have isolated solid compounds $M(acac)_3(CHCl_3)_2$ (M = Al, Cr, and Fe), and from a preliminary *X*-ray analysis suggested that the two chloroform molecules aligned themselves along the 3-fold inversion axis of the complex, with their hydrogen atoms directed at the chelating oxygens. They estimated that the enthalpies of solvation were: $Al(acac)_3$, 4·8; $Cr(acac)_3$, 4·9; and $Fe(acac)_3$, 5·1 kcal mol^{-1}.

The enthalpies of solution in Table 1 confirm that the proton on the 3-carbon atom of acetylacetone is not

---

[10] T. P. Melia and R. Merrifield, *J. Inorg. Nuclear Chem.*, 1970, **32**, 2573.

[11] W. A. Frankhauser, *U.S. Res. Development Reports*, 1965, **4**, 35.

[12] P. D. Hopkins and B. E. Douglas, *Inorg. Chem.*, 1964, **3**, 357.

[13] J. P. Fackler, jun., T. S. Davis, and I. D. Chawla, *Inorg. Chem.*, 1965, **4**, 130.

[14] J. F. Steinbach and J. H. Burns, *J. Amer. Chem. Soc.*, 1958, **80**, 1839.

important in specific interactions since its replacement by CH_3 in the Al complex has little effect on the result.

As the enthalpies of solution in acetone and benzene are small and positive for the complexes studied, the solvation can be regarded as non-specific and due primarily to dispersion forces. For each of the complexes, negative enthalpies of solvation are in the order acetone $<$ benzene $\ll$ chloroform and this extra exothermicity in chloroform, *ca.* 6 kcal mol^{-1} of solute, can be regarded as a measure of its specific interaction (Table 2). These results suggest that Steinbach's model applies in solution and that two chloroform molecules are hydrogen bonded to each solute molecule.

[3/741 *Received*, 9*th April*, 1973]