Thermochemistry of Beryllium β-Diketonates and Be–O Bond Energies

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Enthalpies of formation of the crystalline complexes of beryllium with 2,2,6,6-tetramethylheptane-3,5-dione (dpm), 1,1,1-trifluoropentane-2,4-dione (tfac), and tropolone, have been determined at 298.15 K by solution calorimetry: ΔH_f°[Be(dpm)$_2$] (c) = −386.5 ± 2.0 kcal mol^{-1}, ΔH_f°[Be(tfac)$_2$] (c) = −597.3 ± 2.0 kcal mol^{-1}, and ΔH_f°[Be(trop)$_2$] (c) = −208.56 ± 0.42 kcal mol^{-1}. Gas phase enthalpies have been calculated and from these the Be–O bond energies have been derived.

IN previous papers [1,2] the standard enthalpies of formation of some tris(β-diketonates) of aluminium(III) and the Al–O bond energies were presented.

Here we examine the corresponding beryllium compounds to compare the ligand effects in a tetrahedral environment.

EXPERIMENTAL

The LKB 8700 Reaction and Solution Precision Calorimeter was used for all solution reactions. The operation and calculation methods have been described before.[2]

Materials.—1,4-*Dioxan*. AnalaR dioxan was purified according to reference 3.

Beryllium sulphate tetrahydrate. This compound (AnalaR) was dried *in vacuo* over phosphorus pentoxide, for 48 h. Its composition was determined by means of beryllium analyses before each set of calorimetric experiments and found to be $BeSO_4 \cdot 4.00OH_2$.

Sulphuric acid. AnalaR sulphuric acid was diluted with water until *ca*. 2.0—2.5M and its concentration was determined by titration against borax. Two batches were prepared and analysed, with the following results: solution 1 : 2.157M($H_2SO_4 \cdot 23.69OH_2$) and solution 2 : 2.500M-($H_2SO_4 \cdot 19.22OH_2$).

Constant-boiling hydrochloric acid. This was prepared from AnalaR HCl by dilution with distilled water. The concentration of the HCl solution was determined by titration against borax. A series of six different determinations gave the result of 4.369M, corresponding to the composition $HCl \cdot 11.60OH_2$.

Perchloric acid (60%). This was analysed against borax, with the following result: 9.207M($HClO_4 \cdot 3.706OH_2$).

Ligands. 2,2,6,6-Tetramethylheptane-3,5-dione (dipivaloylmethane, Hdpm), 1,1,1-trifluoropentane-2,4-dione (trifluoroacetylacetone, Htfac), and tropolone (Htrop) were prepared and purified as described previously.[1,2]

Bis(2,2,6,6-*tetramethylheptane*-3,5-*dionato*)*beryllium*(II), [Be(dpm)$_2$]. This was prepared by the method of Hammond *et al.*[4] A solution of Hdpm in ethanol was mixed with a solution of beryllium acetate in water, concentrated aqueous ammonia being added dropwise, with stirring. The product gradually separated, was filtered off, dried, recrystallised from acetone, and sublimed *in vacuo*, m.p. 92—94 °C (lit.,[4] 93—97 °C and lit.,[5] 95—97 °C) (Found: C, 70.2; H, 10.2; Be, 2.4. Calc. for $C_{22}H_{38}BeO_4$: C, 70.4; H, 10.20; Be, 2.40%).

Bis(*trifluoroacetylacetonato*)*beryllium*(II), [Be(tfac)$_2$]. Trifluoroacetylacetone was suspended in water and 2M-aqueous ammonia was added dropwise until an almost clear solution was obtained; a small amount of ethanol was added and this was followed by 2M-hydrochloric acid, added dropwise, until neutral pH was obtained. This solution was mixed and stirred with a solution of AnalaR beryllium sulphate in water. The white precipitate was filtered off, dried, and twice sublimed *in vacuo*,[6] m.p. 112 °C (Found: C, 38.15; H, 2.55; Be, 2.85. Calc. for $C_{10}H_8F_6BeO_4$: C, 38.1; H, 2.56; Be, 2.86%).

Bis(*tropolonato*)*beryllium*(II), [Be(trop)$_2$]. This was prepared by adding a solution of AnalaR beryllium sulphate in water to a solution of tropolone in ethanol. The mixture

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[1] R. J. Irving and M. A. V. Ribeiro da Silva, *J.C.S. Dalton*, 1976, 1940.

[2] R. J. Irving and M. A. V. Ribeiro da Silva, *J.C.S. Dalton*, 1975, 1257.

[3] J. O. Hill and R. J. Irving, *J. Chem. Soc.* (*A*), **1966**, 971.

[4] G. S. Hammond, D. C. Nonhebel, and C. H. S. Wu, *Inorg. Chem.*, 1963, **2**, 73.

[5] E. W. Berg and N. M. Herrera, *Analyt. Chim. Acta*, 1972, **60**, 117.

[6] A. Arch and R. C. Young, 'Inorganic Synthesis,' ed. W. C. Fernelius, McGraw-Hill, New York, 1946, p. 17.

was heated on a steam-bath and a few drops of 2M-aqueous ammonia were added. The off-white precipitate was filtered off, washed with water, dried, and recrystallised twice from chloroform–light petroleum (b.p. 60—80 °C), m.p. 209—210 °C (Found: C, 66.9; H, 4.05; Be, 3.55. Calc. for $C_{14}H_{10}BeO_4$: C, 66.9; H, 4.01; Be, 3.59%).

Analyses.—All carbon and hydrogen analyses were carried out in the Microanalytical Service of the University of Surrey; beryllium was analysed by conversion into the oxide BeO.

Method for Solution Calorimetry.—Decomposition of the complexes into metal ion and free ligand was extremely slow in dilute acid solutions but satisfactory results could be obtained using a mixture of 4.4M-HCl (25%) and dioxan (75%) for the dipivaloylmethane and trifluoroacetylacetone complexes, and 60% perchloric acid for the tropolone complex.

RESULTS AND DISCUSSION

The standard enthalpy of formation of the different beryllium complexes, can be determined from the reaction between the different ligands (HL) and beryllium sulphate.

$$2\mathrm{HL(l\ or\ c)} + \mathrm{BeSO_4{\cdot}4OH_2} \xrightarrow{\Delta H_R} \mathrm{H_2SO_4{\cdot}4OH_2} + [\mathrm{BeL_2}]$$

The difference between the enthalpies of solution of the products and reactants in the same stoicheiometric ratio, gives the required enthalpy of formation, provided equilibrium is reached from either side within the period of the experiment.

$$\begin{tikzcd}
\mathrm{BeSO_4{\cdot}4OH_2\ (c)} \arrow[d, "\Delta H_3"] & +\ 2\mathrm{HL\ (l)} \arrow[d, "\Delta H_2"] & +\ 19.69\mathrm{OH_2\ (l)} \arrow[d, "\Delta H_1"] \arrow[r, "\Delta H_R"] & {[\mathrm{BeL_2}]\ \mathrm{(c)}} \arrow[d, "\Delta H_5"] & +\ \mathrm{H_2SO_4{\cdot}23.69OH_2\ (l)} \arrow[d, "\Delta H_4"] \\
\text{Solvent} & \text{(75\% dioxan/25\%} & \text{4.4M-HCl)} & \text{Solvent} & \text{(75\% dioxan/25\% 4.4M-HCl)}
\end{tikzcd}$$

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

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

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

$$\text{Solution } A_2 + \mathrm{BeSO_4{\cdot}4OH_2} \xrightarrow{\Delta H_3} \text{Solution } A_3$$

$$\text{Solvent} + \mathrm{H_2SO_4{\cdot}23.69OH_2} \xrightarrow{\Delta H_4} \text{Solution } B_1$$

$$\text{Solution } B_1 + [\mathrm{BeL_2}] \xrightarrow{\Delta H_5} \text{Solution } B_2$$

$$\Delta H_R = 19.69\,\Delta H_1 + 2\Delta H_2 + \Delta H_3 - \Delta H_4 - \Delta H_5 + \Delta H_6$$

SCHEME

To 100.0 cm^3 of calorimetric solvent, ampoules of water, ligand, and beryllium sulphate tetrahydrate were added consecutively and ΔH_1, ΔH_2, and ΔH_3 were measured. To a second portion of the same solvent (100.0 cm^3), were added consecutively ampoules of sulphuric acid and beryllium complex, and ΔH_4 and ΔH_5 were measured. The thermochemical cycle and the general procedure used with the beryllium complexes of dipivaloylmethane and trifluoroacetylacetone is given in the Scheme; for the tropolonate the acid was $\mathrm{H_2SO_4{\cdot}19.22OH_2}$ so the quantity of water for the determination of ΔH_1 was adjusted accordingly.

The quantities of reactants in a particular series of experiments were determined by the amount of beryllium complex in the particular ampoule; strict control of stoicheiometry was maintained throughout each series.

If this procedure is used, the value calculated for ΔH_R will refer 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 solution A_3 in the calorimeter; no heat change was detected.

Thermochemical functions are expressed in terms of 'thermochemical calories' (1 thermochemical calorie = 4.184 J) and refer to the isothermal process at 298.15 K. The uncertainty interval is twice the standard deviation of the mean.

The experimental data for the different compounds studied are presented in Tables 1—3 leading to the following ΔH_R of $+4.47 \pm 0.41$ kcal mol^{-1} for [Be(dpm)$_2$], -0.5 ± 0.42 kcal mol^{-1} for [Be(tfac)$_2$], and $+4.40 \pm 0.06$ kcal mol^{-1} for [Be(trop)$_2$].

From the literature values, ΔH_f° $\mathrm{BeSO_4{\cdot}4OH_2}$ (c) = -579.29 kcal mol^{-1} (ref. 7), ΔH_f° $\mathrm{H_2SO_4{\cdot}4OH_2}$ (aq) = -480.688 kcal mol^{-1} (ref. 8) and from the standard enthalpies of formation and vaporisation of the different ligands (Table 4), the standard enthalpies of formation of the crystalline complexes were calculated. They are given in Table 5, together with their molar enthalpies of sublimation and consequent molar enthalpies of formation in the gaseous state.

As discussed previously[1,2] the metal–oxygen bond strength can be represented by the following radical gas equation:

$$\mathrm{Be(g)} + 2\mathrm{L{\cdot}(g)} \xrightarrow{\Delta H_{f(r)}} [\mathrm{BeL_2}]\mathrm{(g)}$$

As the oxygen atoms in β-diketonates are known to be

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[7] V. B. Parker, D. D. Wagman, and W. H. Evans, 'Selected Values of Chemical Thermodynamic Properties,' Technical Note 270-6, U.S. Nat. Bur. Standards, Washington, 1971.

[8] D. D. Wagman, W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey, and R. H. Schumm, 'Selected Values of Chemical Thermodynamics Properties,' Technical Note 270-3, U.S. Nat. Bur. Standards, Washington, 1968.

equivalent[9] the homolytic beryllium–oxygen bond energy can be equated to 1/4 of this enthalpy of reaction, *i.e.* $E(\text{Be–O}) = -\frac{1}{4}\Delta H_{f(r)}$.

TABLE 1

Calorimetric study of $[\text{Be(dpm)}_2]$

(*a*) Addition of H_2O to solvent (dioxan–HCl)

H_2O (10^3 amount/mol)	$10^4(\Delta R/R_m)$	ε	ΔH/kcal mol^{-1}
4.8329	6.5534	1615.0	−0.219
5.0988	6.7591	1644.5	−0.218

As the solvent used in this reaction has the same composition as that used for the determination of the standard enthalpies of formation of tris(trifluoroacetylacetonato)aluminium(III) [1] and bis(dipivaloylmethanato)nickel(II),* and the enthalpy of solution of water was found to have the same value as determined before, the values were combined, giving $\Delta H_1 = -0.22 \pm 0.02$ kcal mol^{-1}.

(*b*) Addition of Hdpm to solution A_1

Hdpm (10^4 amount/mol)	$10^4(\Delta R/R_m)$	ε	ΔH/kcal mol^{-1}
4.9110	8.1421	1640.6	+2.720
5.2718	8.1455	1759.8	+2.719

As these results are the same as those determined during the study of the standard enthalpy of formation of bis(dipivaloylmethanato)nickel(II),* it was decided to adopt here the previously determined value, so, $\Delta H_2 = +2.74 \pm 0.04$ kcal mol^{-1}.

(*c*) Addition of $BeSO_4{\cdot}4OH_2$ to solution A_2

$BeSO_4{\cdot}4OH_2$ (10^4 amount/mol)	$10^4(\Delta R/R_m)$	ε	ΔH/kcal mol^{-1}
2.4953	4.8115	1642.6	+3.167
2.5162	4.9471	1628.7	+3.202
2.5037	4.9761	1656.9	+3.293
2.5054	4.8976	1631.5	+3.189
2.5162	4.8869	1626.5	+3.159

Mean: $\Delta H_3 = +3.20 \pm 0.05$ kcal mol^{-1}

(*d*) Addition of $H_2SO_4{\cdot}23.69OH_2$ to solvent (dioxan–HCl)

$H_2SO_4{\cdot}23.69\ OH_2$ (10^4 amount/mol)	$10^4(\Delta R/R_m)$	ε	ΔH/kcal mol^{-1}
2.4925	9.1421	1643.1	−6.026
2.5331	9.3738	1634.1	−6.047
2.4977	9.0916	1640.8	−5.973
2.5049	9.2469	1656.0	−6.113
2.5577	9.4337	1626.7	−6.000

Mean: $\Delta H_4 = -6.03 \pm 0.05$ kcal mol^{-1}

(*e*) Addition of $[\text{Be(dpm)}_2]$ to solution B_1

$[\text{Be(dpm)}_2]$ (10^4 amount/mol)	$10^4(\Delta R/R_m)$	ε	ΔH/kcal mol^{-1}
2.4910	9.0938	1609.9	+5.877
2.5325	9.3506	1621.5	+5.987
2.4968	8.7875	1663.2	+5.854
2.5011	8.8458	1643.2	+5.812
2.5581	9.2978	1650.7	+6.000

Mean: $\Delta H_5 = +5.91 \pm 0.07$ kcal mol^{-1}

* R. J. Irving and M. A. V. Ribeiro da Silva, unpublished work.

It has been shown [1,3] that it is reasonable to assume a value of 100 ± 5 kcal mol^{-1} for the dissociation energy of the enolic hydrogen from the considered parent β-keto-enolates and that for tropolone a value of 90 ± 5 kcal mol^{-1} is more appropriate.[2] On this assumption, and using the value of ΔH_f° H· (g) = 52.095 kcal mol^{-1} (ref. 8), the enthalpies of formation of the gaseous free radicals of the different ligands were calculated: ΔH_f° pd· (g) = −43.6 ± 5.0 kcal mol^{-1} (ref. 1), ΔH_f° dpm· (g) = −84.1 ± 5.1 kcal mol^{-1} (ref. 1), ΔH_f° tfac· (g) = 192.5 ± 5.1 kcal mol^{-1} (ref. 1), and ΔH_f° trop· (g) = +1 ± 5 kcal mol^{-1} (ref. 2). Since ΔH_f° Be (g) = 77.5 kcal mol^{-1} (ref. 7), the values of $\Delta H_{f(r)}^\circ$ for the formation reaction of the different complexes were calculated and hence the homolytic beryllium–oxygen bond energy values, $E(\text{Be–O})$ as defined by the radical gas reaction. These values are given in Table 6.

TABLE 2

Calorimetric study of $[\text{Be(tfac)}_2]$

(*a*) Addition of H_2O to solvent (dioxan–HCl)

H_2O (10^3 amount/mol)	$10^4(\Delta R/R_m)$	ε	ΔH/kcal mol^{-1}
4.9406	6.5824	1650.5	−0.220
4.9162	6.2358	1615.9	−0.205

These values agree very well (within the experimental error) with the one found for the same reaction in the study of $[\text{Be(dpm)}_2]$. Therefore, the value determined previously [1] for a set of five experiments was adopted, so $\Delta H_1 = -0.22 \pm 0.02$ kcal mol^{-1}.

(*b*) Addition of Htfac to solution A_1

Htfac (10^4 amount/mol)	$10^3(\Delta R/R_m)$	ε	ΔH/kcal mol^{-1}
5.0211	1.6629	1654.6	−5.480
4.9964	1.7159	1601.5	−5.500

These values are also in excellent agreement with the ones found for a similar reaction in the study of tris(trifluoroacetylacetonato)-aluminium(III) [1] so the value found before in a series of six determinations was taken: $\Delta H_2 = -5.49 \pm 0.06$ kcal mol^{-1}.

(*c*) Addition of $BeSO_4{\cdot}4OH_2$ to solution A_2

$BeSO_4{\cdot}4OH_2$ (10^4 amount/mol)	$10^4(\Delta R/R_m)$	ε	ΔH/kcal mol^{-1}
2.5105	4.8131	1596.3	+3.060
2.4981	4.6811	1595.3	+2.989
2.4964	4.7856	1602.1	+3.071
2.5054	4.8746	1607.5	+3.128
2.4834	4.6738	1609.9	+3.030

Mean: $\Delta H_3 = +3.06 \pm 0.05$ kcal mol^{-1}

(*d*) Addition of $H_2SO_4{\cdot}23.69OH_2$ to solvent (dioxan–HCl)

$H_2SO_4{\cdot}23.69OH_2$ (10^4 amount/mol)	$10^4(\Delta R/R_m)$	ε	ΔH/kcal mol^{-1}
2.4996	9.2219	1624.1	−5.992
2.4958	9.1069	1661.8	−6.064

These values fall inside the experimental error of the value found for the same reaction in the study of bis(dipivaloylmethanato)beryllium(II) and this supports the experimental results obtained before during the solution reaction of H_2O. As a result of this, the value found before for a set of five experiments was taken, and so $\Delta H_4 = 6.03 \pm 0.05$ kcal mol^{-1}.

(*e*) Addition of $[\text{Be(tfac)}_2]$ to solution B_1

$[\text{Be(tfac)}_2]$ (10^4 amount/mol)	$10^4(\Delta R/R_m)$	ε	ΔH/kcal mol^{-1}
2.4996	9.7143	1593.1	−6.191
2.4958	9.7474	1601.8	−6.256
2.5002	9.5592	1605.3	−6.138
2.5053	9.5892	1589.2	−6.083
2.4916	9.5995	1608.0	−6.195

Mean: $\Delta H_5 = -6.17 \pm 0.06$ kcal mol^{-1}

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[9] E. C. Lingafelter and R. L. Braun, *J. Amer. Chem. Soc.*, 1966, **88**, 2951.

TABLE 3

Calorimetric study of [Be(trop)$_2$]

(*a*) Addition of H_2O to solvent ($HClO_4\cdot3.706OH_2$)

The value of ΔH_1 was calculated from the literature data,[8] $\Delta H_1 = 1.429 \pm 0.001$ kcal mol^{-1}, and was found to be in good agreement with some experimental data obtained in this laboratory.*

(*b*) Addition of $BeSO_4\cdot4OH_2$ to solution A_1

$BeSO_4\cdot4OH_2$ (10^4 amount/mol)	$10^3(\Delta R/R_m)$	ε	ΔH/kcal mol^{-1}
5.4913	2.6592	2144.1	+10.383
5.2604	2.7244	1994.5	+10.330
5.0933	2.4644	2136.7	+10.338
4.9279	2.4058	2109.3	+10.298
5.1655	2.4982	2128.8	+10.295

Mean: $\Delta H_2 = +10.33 \pm 0.03$ kcal mol^{-1}

(*c*) Addition of Htrop to solution A_2

Htrop (10^4 amount/mol)	$10^4(\Delta R/R_m)$	ε	ΔH/kcal mol^{-1}
10.9822	9.7255	2055.6	−1.821
10.5220	9.0241	2113.9	−1.813
9.8547	8.6170	2115.8	−1.850
9.7662	8.1010	2141.7	−1.777
10.3304	8.7109	2135.1	−1.800

Mean: $\Delta H_3 = -1.81 \pm 0.02$ kcal mol^{-1}

(*d*) Addition of $H_2SO_4\cdot19.22OH_2$ to solvent ($HClO_4\cdot3.706OH_2$)

$H_2SO_4\cdot19.22OH_2$ (10^4 amount/mol)	$10^3(\Delta R/R_m)$	ε	ΔH/kcal mol^{-1}
5.4721	3.7358	2129.7	−14.540
5.3180	3.6337	2135.8	−14.594
5.1033	3.4675	2146.2	−14.583
4.9353	3.3583	2133.8	−14.520
5.0119	3.4161	2143.7	−14.611

Mean: $\Delta H_4 = -14.57 \pm 0.03$ kcal mol^{-1}

(*e*) Addition of [Be(trop)$_2$] to solution B_1

[Be(trop)$_2$] (10^4 amount/mol)	$10^3(\Delta R/R_m)$	ε	ΔH/kcal mol^{-1}
5.4787	1.3194	2135.3	−5.142
5.3259	1.2926	2135.2	−5.182
4.9891	1.2090	2125.2	−5.150
4.9378	1.2129	2105.5	−5.172
5.1034	1.2419	2130.4	−5.185

Mean: $\Delta H_5 = -5.17 \pm 0.02$ kcal mol^{-1}

* R. J. Irving and G. Walter, *J. Chem. Soc.* (*A*), 1969, 2690.

TABLE 4 *

Ligand	ΔH_f°(l)	ΔH°(vap.)	ΔH_f°(g)
Hpd (keto-enol) †	-101.29 ± 0.37 [a,b]	$+9.99 \pm 0.05$ [d]	-91.30 ± 0.37
Hdpm	-146.2 ± 1.0	$+14.23 \pm 0.03$ [e]	-132.0 ± 1.0 [g]
Htfac	-249.3 ± 1.0	$+8.90 \pm 0.04$ [e]	-240.4 ± 1.0 [g]
Htrop (c)	-57.18 ± 0.21 [a,c]	$+20.1 \pm 0.1$(subl.)	-37.08 ± 0.23

* All values in kcal mol^{-1}. † Hpd = pentane-2,4-dione.

[a] J. D. Cox and G. Pilcher, 'Thermochemistry of Organic and Organometallic Compounds,' Academic Press, London, 1970. [b] G. R. Nicholson, *J. Chem. Soc.*, 1957, 2431. [c] W. N. Hubbart, C. Katz, G. B. Guthrie, jun., and G. Waddington, *J. Amer. Chem. Soc.*, 1952, **74**, 4456. [d] R. J. Irving and I. Wadso, *Acta Chem. Scand.*, 1970, **24**, 589. [e] R. J. Irving and M. A. V. Ribeiro da Silva, *J.C.S. Dalton*, 1975, 798. [f] W. Jackson, T. S. Hung, and H. P. Hopkins, jun., *J. Chem. Thermodynamics*, 1971, **3**, 347. [g] Estimated by the Laidler method (M. A. V. Ribeiro da Silva, Ph.D. Thesis, University of Surrey, 1973).

The heterolytic beryllium–oxygen bond energies were calculated for the reaction

$$Be^{2+}\,(g) + 2L^-\,(g) \xrightarrow{\Delta H_{f(i)}} [BeL_2]\,(g)$$

on the same assumption as before.[1,2] From the values ΔH_f° acac$^-$ (g) = -77.4 ± 5 kcal mol^{-1} (ref. 1), ΔH_f°-dpm$^-$ (g) = -116.9 ± 5 kcal mol^{-1} (ref. 1), ΔH_f° tfac$^-$ (g) = -225.3 ± 5 kcal mol^{-1} (ref. 1), and ΔH_f° trop$^-$ (g) = -33 ± 5 kcal mol^{-1} (ref. 2) and ΔH_f° Be^{2+} (g) = 715.4 kcal mol^{-1} (ref. 7), values of $\Delta H_{f(i)}$ for the ionic gas formation reaction of the different complexes were calculated and hence the so-called heterolytic beryllium–oxygen bond energy values, E'(Be–O), as defined by the ionic gas reaction (Table 6).

As noted previously,[1,2] in attempting a rigorous determination of bond energies, estimates of some enthalpies of formation and sublimation have had to be made, as well as the dissociation energy of the enolic hydrogen from the parent β-ketoenolates. The resulting bond energies, therefore, have a large uncertainty attached to them.

The stability of a co-ordination compound is commonly interpreted as referring to the process

$$M^{n+} + nL^- \longrightarrow [ML_n]$$

occurring in solution and as this is a Lewis acid-base reaction, the stability of the compound should increase as the strength of the Lewis base increases. One would expect therefore that the stability should be in the order of increasing dissociation constant (p*K*) of the ketone, *i.e.* trifluoroacetylacetone (6.8),[10] tropolone (7.0),[11] acetylacetone (9.0),[12] and dipivaloylmethane (11.8).[13] What little data there are from 'stability constant' studies support this: beryllium tropolonate[14] and beryllium acetylacetonate[15] have overall stability constants of 15.4 and 16.7 respectively in 50% dioxan from which the free energies can be derived: ΔG[Be(trop)$_2$] = −21.0 and ΔG[Be(pd)$_2$] = −22.8 kcal mol^{-1}.

This is a significant difference in free energy but there is no way of calculating the corresponding enthalpy of reaction for [Be(trop)$_2$] to compare it with the experimentally determined enthalpy of formation of [Be(pd)$_2$] (−8.9 kcal mol^{-1}), in solution.

The enthalpy of formation of beryllium acetylacetonate from its ions in the vapour state is −836 kcal mol^{-1} showing the overriding importance of solvation effects in solution processes. It is apparent from this, that

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[10] S. P. Patel, Ph.D. Thesis, University of Surrey, 1973.

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[13] G. A. Guter and G. S. Hammond, *J. Amer. Chem. Soc.*, 1956, **78**, 5166.

[14] B. E. Bryant, W. C. Fernelius, and B. E. Douglas, *J. Amer. Chem. Soc.*, 1953, **75**, 3784.

[15] B. E. Bryant, and W. C. Fernelius, *J. Amer. Chem. Soc.*, 1954, **76**, 1695.

TABLE 5 *

Complex	ΔH_f° (c)	ΔH° (subl.)	ΔH_f° (g)
$[Be(pd)_2]$	−298.06 ± 0.62 [a]	22.14 ± 0.50 [b]	−275.92 ± 0.80
$[Be(dpm)_2]$	−386.5 ± 2.0	24.66 ± 0.74 [b]	−361.8 ± 2.1
$[Be(tfac)_2]$	−597.3 ± 2.0	22.98 ± 0.56 [b]	−574.3 ± 2.1
$[Be(trop)_2]$	−208.56 ± 0.42	25.0 ± 5.0 [c]	−183.6 ± 5.0

* All values in kcal mol^{-1}.

[a] R. J. Irving, unpublished work. [b] R. J. Irving and H. Naghibi, unpublished work. [c] Estimated (R. J. Irving and M. A. V. Ribeiro da Silva, *J.C.S. Dalton*, 1975, 798).

TABLE 6 *

Complex	$\Delta H_{f(r)}$	E (M–O)	$\Delta H_{f(i)}$	E' (M–O)
$[Be(pd)_2]$	−266 ± 10	67 ± 3	−836 ± 10	209 ± 3
$[Be(dpm)_2]$	−271 ± 10	67 ± 3	−843 ± 10	211 ± 3
$[Be(tfac)_2]$	−267 ± 10	67 ± 3	−839 ± 10	210 ± 3
$[Be(trop)_2]$	−263 ± 11	66 ± 3	−833 ± 11	208 ± 3
$[Al(pd)_3]$ [a]	−347 ± 15	58 ± 3	−1 478 ± 15	246 ± 3
$[Al(dpm)_3]$ [b]	−369 ± 15	61 ± 3	−1 503 ± 15	250 ± 3
$[Al(tfac)_3]$ [b]	−368 ± 15	61 ± 3	−1 502 ± 15	250 ± 3
$[Al(trop)_3]$ [b]	−368 ± 15	61 ± 3	−1 468 ± 15	250 ± 3
$[Al(4\text{-}Metrop)_3]$ [a]	−357 ± 15	60 ± 3	−1 487 ± 15	248 ± 3

* All values in kcal mol^{-1}.

[a] From ref. 2. [b] From ref 1.

stability constants can give very little direct indication of metal–ligand bond energies.

Whether the M–L bond energy is expressed in terms of dissociation into radicals or ions, the uncertainty arising from the use of estimated auxillary data is sufficiently large to obscure any clear-cut effect of ligand parameters on the bond energies, but it is noteworthy that a change in dissociation constant of ligand from pK 6.8 to 11.8 causes a change in the heterolytic bond energy of less than 4 kcal (2%).

In comparing the bond strengths between corresponding beryllium and aluminium compounds the approximations in the bond energies are constant so that differences become real, and for each ligand the Be–O bond is some 6 kcal stronger than the Al–O bond.

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