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is extremely facile for $n \geq 6$, we suggest that for the $CH_3O(CH_2)_nOCH_3-Fe^+$ complexes for $n \geq 6$ dehydrogenation involves the *central* part of the methylene chain. While this has not yet been demonstrated explicitly for the higher α,ω-dimethoxyalkanes, it should be recalled that a recent detailed study of regio- and stereospecifically labeled isotopomers of $HO(CH_2)_8OH$ is fully in line with this proposal.[9c] This finding is a further demonstration for what has been amply demonstrated in the present study: *The gas-phase chemistry of organometallic systems is extremely dependent upon the directionality*[21,22] *available to the complexed metal ions.* Any rules and qualitative concepts which would enable us to describe the interplay of a given metal ion M^+ with a functional group and the mechanism of folding back the alkyl chain will greatly enhance the chances to correctly predict which segment of a flexible alkyl chain is likely to be activated via oxidative addition processes. Major efforts by theoreticians are indicated to provide this information which, no doubt, will significantly add to a better understanding of organometallic processes in general.

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Metal–Ligand Bond Energies and Solvation Energies for Gas-Phase Transition-Metal Tris(acetylacetonate) Complexes and Their Negative Ions

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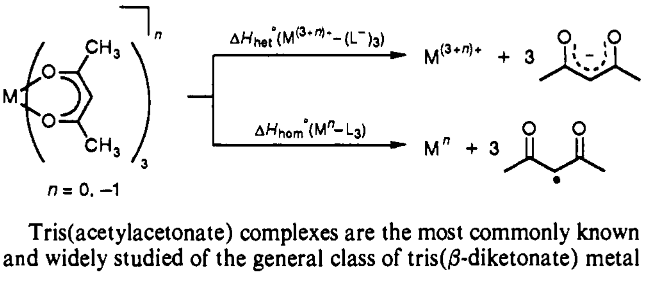
Abstract: The gas-phase bond disruption enthalpies and solvation free energies for several tris(acetylacetonate) transition metal(III) complexes ($M(acac)_3$) and their metal(II) anions are derived from the results of Fourier transform ion cyclotron resonance (FTICR) studies of electron attachment to the complexes and the acetylacetonyl radical (acac). New values are reported for the average M–O bond disruption enthalpies, both homolytic ($\Delta H^\circ_{hom}(M–O)$) and heterolytic ($\Delta H^\circ_{het}(M–O)$), for $M(acac)_3$ with M = Cr, Mn, Fe, and Co. The values of $\Delta H^\circ_{hom}(M–O)$ are reevaluations of earlier results obtained from reaction calorimetry and are based on new experimental data for the electron attachment energy of acetylacetonyl radical ($C_5H_7O_2^\bullet$) determined by Fourier transform mass spectrometry (-58 ± 3 kcal mol^{-1}) and a new value derived for the homolytic O–H bond dissociation enthalpy in the enol form of acetylacetone (88 ± 6 kcal mol^{-1}). From the gas-phase electron attachment free energies for a series of $M(acac)_3$ complexes ($\Delta G^\circ_a(M(acac)_3,g)$) for M = Cr, Mn, Fe, Co, a thermodynamic cycle is used to obtain average $\Delta H^\circ_{het}(M–O)$ values for the corresponding gas-phase anionic $M(acac)_3^-$ complexes. For the $M(acac)_3(g)$ complexes of the metals Cr, Mn, Fe, and Co, respectively, the following mean bond disruption enthalpies (kcal mol^{-1}) are obtained: $\Delta H^\circ_{hom}(M–O) = 45 \pm 3, 33 \pm 3, 36 \pm 3, 33 \pm 3$; $\Delta H^\circ_{het}(M–O) = 224 \pm 5, 222 \pm 5, 217 \pm 5, 228 \pm 5$. For the $M(acac)_3^-(g)$ anions the following mean bond disruption enthalpies are obtained for M = Cr, Mn, Fe, Co, respectively: $\Delta H^\circ_{hom}(M–O) = 46 \pm 3, >43, 43 \pm 3, 38 \pm 4$; $\Delta H^\circ_{het}(M–O) = 108 \pm 8, 103 \pm 8, 107 \pm 8, 107 \pm 8$. The $\Delta G^\circ_a(M(acac)_3,g)$ values for several complexes combined with estimates of single electrode potentials for the same $M(acac)_3^{0/-}$ couples in solution are used to obtain the change in solvation free energies ($\Delta\Delta G^\circ_{solv}$) for these couples in acetonitrile. Values of $\Delta\Delta G^\circ_{solv}$ obtained are in the range of -50 ± 5 kcal mol^{-1} for couples involving first-row transition metals. These assessments of bond energies and solvation energies based on gas-phase electron attachment energies lead to a complete quantitative interpretation of the observed solution electrode potentials for the $M(acac)_3$ complexes studied.

Introduction

We recently used Fourier transform ion cyclotron resonance (FTICR) to obtain data leading to values for the free energy of gas-phase electron attachment (ΔG°_a) for the series of volatile tris(acetylacetonate) complexes ($M(acac)_3$) for the metals M = Ti, V, Cr, Mn, Fe, Co, and Ru.[1,2] Estimates of ΔG°_a values were also obtained for the tris(hexafluoroacetylacetonate) complexes of the metals Sc–Co and Ga.[1,2] The ΔG°_a values were obtained for the $M(acac)_3$ complexes by using electron-transfer (or "charge-transfer") equilibrium techniques that have previously been used to generate electron attachment thermodynamics primarily for organic compounds.[3] From the data obtained earlier[1] and new results of FTICR studies, we report here the first extensive analysis of gas-phase bond disruption enthalpies and relative solvation free energies for both oxidation states in a class of transition metal coordination complex redox couples.

Scheme I



Tris(acetylacetonate) complexes are the most commonly known and widely studied of the general class of tris(β-diketonate) metal

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† A. P. Sloan Foundation Research Fellow, 1988–1990.

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Scheme II

$$\text{(a)}\quad A^- + B \longrightarrow A + B^-$$
$$\text{(b)}\quad B^- + C \longrightarrow B + C^-$$

complexes.[4] In recent years, they have become popular as volatile sources of metals in chemical vapor deposition approaches to the preparation of ceramic superconductors.[5] Despite the widespread study of the chemical and electronic properties of acetylacetonate (acac$^-$) metal complexes, accurate thermochemical data are somewhat meager. In the cycles used to obtain homolytic and heterolytic bond disruption enthalpies for M(acac)$_3$ complexes, the value for the homolytic bond dissociation enthalpy of the enolic O–H bond in acetylacetone introduces the greatest uncertainty since no experimental data pertaining to this bond energy are available. From the results of thermal gas-phase charge-transfer reactions involving acac$^-$ ions, an improved estimate is made here for the enolic O–H bond enthalpy. From the original reaction calorimetry data, improved estimates are made for the M–O homolytic and heterolytic bond disruption enthalpies ($\Delta H^\circ_{\text{hom}}$ and $\Delta H^\circ_{\text{het}}$) for M(acac)$_3$ complexes (Scheme I, $n = 0$). When combined with the gas-phase electron attachment data for the M(acac)$_3$ complexes,[1] these results also lead to the heterolytic and homolytic bond disruption enthalpies for the corresponding gas-phase M(acac)$_3^-$ ions (Scheme I, $n = -1$).

Reliable data for deducing solvation energies of complex metal ions are scarce yet are essential for a complete understanding of the thermodynamics of redox processes at coordinated metal centers. The FTICR data[1] for M(acac)$_3$ complexes are used here to obtain the first experimentally based assessment of solvation energetics for a series of transition metal coordination complexes with a common ligand environment. Several of the M(acac)$_3$ complexes for which gas-phase electron attachment data were obtained also exhibit reversible electrochemical behavior for one electron reduction. From $E_{1/2}$ data, estimates of single electrode potentials are made, and, when these values are combined with the gas-phase data, differential solvation free energies for several M(acac)$_3^{0/-}$ couples are obtained. Consideration of the relative contributions of the changes in solvation energies and bond energies that occur for electron attachment to M(acac)$_3$ complexes provides an overall appreciation of their thermochemical contributions to the magnitude of a particular M(acac)$_3^{0/-}$ electrode potential.

Experimental Section

Electron Attachment Studies. Gas-phase electron-transfer reactions were studied by using a Nicolet FT/MS 1000 Fourier transform ion cyclotron resonance mass spectrometer.[6] The free energy of electron capture by acetylacetonyl radical $C_5H_7O_2^\bullet$ (acac$^\bullet$) at 350 K was determined by gas-phase electron-transfer bracketing.[3] For the general case shown in Scheme II, involving the species B for which the electron attachment energy is to be determined, the observation of the two separate charge-transfer reactions gives the order of gas-phase ΔG°_a values as $\Delta G^\circ_a(C) < \Delta G^\circ_a(B) < \Delta G^\circ_a(A)$. Known electron attachment free energies of A and C set the upper and lower limits for the value for B. For some half-reactions, such as B = acac$^{0/-}$, the pressure of the neutral species cannot be fixed, and only reactions b in Scheme II can be followed. In such a case, the absence of a measurable rate for a particular acceptor is taken as an indication that the electron affinity of B is higher than that of C.

Table I. Free Energies[a] of Electron Attachment to M(acac)$_3$ Complexes and Enthalpies[a] of Electron Attachment to Free M^{3+}(g) Ions and M(g)

M	ΔG°_a(M(acac)$_3$)	ΔH°_a(M^{3+}(g))[b]	ΔH°_a(M(g))[e]
Ti	<0	−633.96	−1.8 (0.3)
V	−24.9 ± 2.4[c]	−675.9	−12 (1)
Cr	−20 ± 3[d]	−713.9	−15 (1)
Mn	−59 ± 5[d]	−776.4	>0
Fe	−43.0 ± 2.4[c]	−706.83	−3.5 (0.1)
Co	−47 ± 4[d]	−772.5	−15.3 (0.1)
Ru	−38.7 ± 2.4[c]	−656.5	−24 (4)

[a] All values in kcal mol^{-1}. Temperature = 350 K for M(acac)$_3$ complexes and 0 K for free ions and atoms. [b] Values given are negative of the third ionization potentials of the metals taken from ref 7. Conversion factor = 23.0605 kcal mol^{-1} eV^{-1}. [c] Value obtained from measured charge-transfer equilibrium constant. See ref 1 and 4. Error limits assume reference compound ΔG°_a values known to ±2.3 kcal mol^{-1}. [d] Value obtained by bracketing (Scheme II). Error limits assume reference compound ΔG°_a values known to ±2 kcal mol^{-1}. [e] Data from: Hotop, H.; Lineberger, W. C. *J. Phys. Chem. Ref. Data* **1985**, *14*, 731. Leopold, D.; Lineberger, W. *J. Chem. Phys.* **1986**, *85*, 51. Number in parentheses is the uncertainty in the last figure(s).

Scheme III

$$\begin{tikzcd}
\text{(a)} & M^{3+}(g) + 3L^-(g) + e^- \arrow[r, "\Delta X_a(M^{3+}, g)"] \arrow[d, "\Delta X_{het}^\circ(M^{3+}-(L^-)_3)", "\text{cycle 1}"'] & M^{2+}(g) + 3L^-(g) \arrow[d, "\Delta X_{het}^\circ(M^{2+}-(L^-)_3)"] \\
\text{(b)} & ML_3(g) + e^- \arrow[r, "\Delta X_a(M_3, g)"] \arrow[d, "\Delta X_{solv}^\circ(ML_3)", "\text{cycle 2}"'] & ML_3^-(g) \arrow[d, "\Delta X_{solv}^\circ(ML_3^-)"] \\
\text{(c)} & ML_3(soln) + e^- \arrow[r, "\Delta X_a(ML_3, soln)"] & ML_3^-(soln)
\end{tikzcd}$$

Acetylacetonate ions were produced by electron capture in a low background pressure (~10^{-7} Torr) of cobalt tris(acetylacetonate) (the parent ion dissociates to form CoL$_2$ + L$^-$).[1] The compound was introduced by using a solids probe at ~100 °C in the FTICR main chamber. Charge-transfer reactions were followed involving acetylacetonate ions and various gaseous organic compounds at a pressure of ~10^{-6} Torr. The organic compounds used were chosen from the volatile organics for which electron attachment energies have been determined in several recent reports.[3a] Thermalization of the ions prior to reaction was ensured by adding a relatively large background pressure of cyclohexane bath gas (~10^{-6} Torr) and allowing a period of 1 s prior to monitoring the electron-transfer reactions. In that time, the ions have ~30 collisions with neutrals, which effectively lowers the ion temperature to that of the neutrals.

Results

The technique used to obtain the free energies of electron attachment to M(acac)$_3$ complexes at ~350 K has been described in detail previously,[1] and Table I gives the results of the electron attachment data for the series of M(acac)$_3$ compounds.[1] Also included in Table I are the electron attachment energies for the corresponding free gaseous M^{3+} ions and M atoms, which are the negative value of the third ionization potentials and electron affinities of the metals, respectively. These values are auxiliary data required in this report and are included here for ease of comparison to the electron attachment energies for the M(acac)$_3$ complexes.

From the studies of electron-transfer reactions of the acetylacetonate ion, ΔG°_a of acac$^\bullet$ could be bracketed over the narrowest energy range by using the reference compounds 2,6-dichlorobenzoquinone (26DCBQ) and tetrafluorobenzoquinone (TFBQ). The values of ΔG°_a at 423 K for these compounds have been determined by Kebarle and co-workers to be −55.8 and −60.9 kcal mol^{-1}, respectively.[3a] The corresponding values for ΔS°_a were also determined and found to be −3.5 eu for both compounds.[3a] The reaction of acac$^-$ with TFBQ was found to be near the Langevin rate, while reaction with 26DCBQ could not be detected. From these data a value of ΔG°_a for acac$^\bullet$ (−59 ± 5 kcal mol^{-1}

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at 350 K) is obtained (error limits are assigned by considering the usual errors associated with the reference compounds).

Discussion

Electron Attachment Energy Relationships. The general thermochemical cycle in Scheme III is the basis for most of the thermochemical results presented in this report. The cycle shows the general thermochemical relationships between changes in the thermodynamic functions X (e.g., $X = G, H$, or S) for M–L bond formation or solvation of a complex and electron attachment thermodynamics (ΔX°_a) for a metal ion in essentially three physically different environments (reactions a, b, and c) at a given temperature. A cycle of this type and crude estimates of the various thermodynamic quantities were discussed by Buckingham and Sargeson,[8] and a recent quantitative discussion of related cycles for some common coordination complexes is available.[2c] In reaction a, electron attachment is to a metal ion M with a 3+ charge in the free gaseous state, $M^{3+}(g)$. In (b), electron attachment is to the gas-phase complex $[ML_3]^0(g)$ in which the metal ion M^{3+} is formally ligated by three equivalent anionic ligands (L^-). In (c) the solvated metal complex is reduced to $[ML_3]^-(soln)$.

In the upper part of Scheme III, labeled cycle 1, the difference in ΔX°_a for the electron attachment reactions a and b, given by $\Delta X^\circ_a(M^{3+},g)$ and $\Delta X^\circ_a(ML_3,g)$, are thermochemically related to the difference in ΔX° for heterolytic disruption of all of the metal–ligand bonds for the oxidized and reduced form of the complex, $\Delta X^\circ_{het}(M^{3+}–(L^-)_3)$ and $\Delta X^\circ_{het}(M^{2+}–(L^-)_3)$. A similar cycle can be used to derive $\Delta\Delta X^\circ_{hom}(M–L_3)$ values for homolytic bond disruption. In cycle 2 the difference in ΔX°_a for the electron attachment reactions $\Delta X^\circ_a(ML_3,g)$ and $\Delta X^\circ_a(ML_3,soln)$ is thermochemically related to the difference between ΔX° for solvation of the oxidized and reduced forms of the complex ($\Delta X^\circ_{solv}(ML_3)$ and $\Delta X^\circ_{solv}(ML_3^-)$).

Experimental results for reaction b in Scheme III here involve electron attachment to a neutral molecule. To incorporate the energies for these processes into thermochemical cycles, the values must be determined under thermal conditions. Such data can be obtained by using mass spectrometry through studies of electron-transfer equilibrium reactions[1–4] and are often used to estimate the adiabatic ionization energies or the electron affinities of polyatomic species (these quantities are strictly the differences between the heats of formation of the neutral and its ion at 0 K).[3] The method can be applied equally well to reactions involving positive or negative ions, but such data for metal complexes are scarce. Vertical ionization data are more widely available for volatile metal complexes from studies of ionization appearance potentials and photoelectron spectroscopy (PES).[9–11] The energy difference between the adiabatic and vertical processes can be relatively small if the geometry of the neutral is similar to that of the ion. For example, the adiabatic ionization energy for ferrocene has recently been estimated as 6.81 eV by FTICR[2b,d] (Mautner[3c] also suggests 6.81 eV from pulsed high-pressure mass spectrometry studies), while the vertical IP value obtained from PES is 6.88 eV.[12]

Significant differences between adiabatic and vertical energies may arise, however, when geometry changes upon electron attachment or ionization are significant, and such substantial rearrangements are common in transition metal complex redox chemistry. For example, the adiabatic ionization energy of manganocene is ~6.2 eV,[13,2b] while the vertical ionization energy obtained for the high-spin ground state by PES is 7.0 eV.[10] For metal complexes, therefore, vertical ionization data can only be used in thermochemical cycles such as Scheme III for those cases where it is known, or can be reasonably assumed, that the geometries of the neutral and the ion are not too dissimilar. It should be noted that even if the 0–0 transition energy (the adiabatic energy) can be obtained from the PES spectrum, a statistical mechanical calculation must be used to derive enthalpy, entropy, and free-energy changes at a given temperature. Spectroscopic data needed for such calculations are often unavailable or incomplete for transition metal complexes. On the other hand, gas-phase electron-transfer equilibrium studies provide data that can be used directly in thermochemical calculations involving ionizations and electron attachments near room temperature.

Combining Gas-Phase Electron Attachment Energies with Other Thermochemical Data. In combining thermal gas-phase electron attachment energy data for $M(acac)_3$ complexes with other thermochemical data, it is useful to know the temperature dependence of ΔG°_a since estimates of thermodynamic parameters at other temperatures can then be made. Studies of charge-transfer equilibria for a variety of organic acceptors (using pulsed high-pressure mass spectrometry) have typically shown only a weak temperature dependence of ΔG°_a. Experimental values of ΔS°_a obtained are typically $<\pm 4$ eu,[14] and so for these compounds $\Delta G^\circ_a \approx \Delta H^\circ_a$ within ~1 kcal mol^{-1} over a wide range of temperatures. Similar temperature-dependent studies have not yet been performed for $M(acac)_3$ complexes, and values of ΔS°_a are unknown. Coordination complexes are chemically too dissimilar to the organic compounds that have been studied to assume that ΔS°_a will also be small in all cases.

We have shown elsewhere[15] by statistical mechanics that gas-phase ΔS_a values for many transition metal complex redox couples are expected to be comparable to those for organic acceptors. Larger entropy changes are expected, however, when unusually large changes in skeletal vibrational frequencies and electronic degeneracy accompany the oxidation state change. Not surprisingly, significant estimated intramolecular entropy changes are found for low-spin $Co^{III}(t_{2g}{}^6e_g{}^0) \rightarrow$ high-spin $Co^{II}(t_{2g}{}^5e_g{}^2)$ octahedral couples.[15] This spin-change is expected to occur for the reduction $Co(acac)_3(g) + e \rightarrow Co(acac)_3^-(g)$, and ΔS°_a for this reaction may also be large. Assuming a typical value[15] of $\Delta S^\circ_a = 20$ eu for Co^{III} complexes in the gas phase, the value for ΔH°_a at 298 K is ~7 kcal mol^{-1} higher than ΔG°_a at 350 K (ΔH°_a is weakly dependent on temperature). For the other $M(acac)_3{}^{0/-}$ couples where less change in vibrational and electronic entropies occur, ΔS°_a should be smaller and similar to the values reported for organic compounds. Experimental evidence for these conclusions can be found in the redox couple reaction entropy studies of Weaver and co-workers,[16–18] who found that ΔS°_{rc} values for Co^{III}/Co^{II} couples in solution are consistently ~22 ± 4 cal mol^{-1} K^{-1} higher than those for Ru^{III}/Ru^{II} couples (both low-spin) with the same ligand environments.

Values for the total metal–ligand heterolytic bond disruption enthalpies for $M(acac)_3$ complexes, $\Delta H^\circ_{het}(M^{3+}–(acac^-)_3)$, of the first transition metal series are found to be ~1300 kcal mol^{-1} (see discussion below). Since values of ΔG°_a at 350 K and ΔH°_a at 298 K for $M(acac)_3$ complexes may differ by several kcal mol^{-1} in the worst case, the percentage error introduced into derived values of $\Delta H^\circ_{het}(M^{2+}–(acac^-)_3)$ as a consequence of using the approximation ΔG°_a (350 K) $\approx \Delta H^\circ_a$ (298 K) is small, since these bond enthalpies have values in the range of ~600–650 kcal mol^{-1} (see below). When quoting an average energy per M–O bond, $\Delta X^\circ_{het}(M–O)$, the error introduced by assuming $\Delta G^\circ_a \approx \Delta H^\circ_a$ is probably ≤ 1 kcal mol^{-1} for all cases.

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Table II. Auxiliary Thermochemical Data for M(acac)$_3$ Complexes and Acetylacetone^a

M	Cr	Mn	Fe	Co
$\Delta H°_{sub}$(M(acac)$_3$)	29.4 ± 0.7^b	28.7 ± 2.4^b	32.3 ± 2.4^b	28.2 ± 1.2^c
$\Delta H°_{sub}$(M)	94.8 ± 1.0^d	67.1 ± 1.0^d	99.5 ± 1.0^d	101.5 ± 1.0^d
$\Delta H°_f$(M(acac)$_3$,cr)	−374.0 ± 2.1^b	−329.6 ± 0.9^b	−314.2 ± 0.7^b	−294.9 ± 0.9^c
$\Delta H°_{hom}$(H−acac,enol)	88 ± 6^e		$\Delta H°_f$(Hacac,l,enol)	−102.2 ± 0.3^g
$\Delta H°_a$(acac$^•$)	−58 ± 5^e		$\Delta H°_f$(H,g)	52.104 ± 0.003^d
$\Delta H°_{vap}$(Hacac,enol)	10.3 ± 0.1^f		$\Delta H°_{pa}$(acac$^-$)	−344 ± 3^h

^{a}All values given in kcal mol^{-1}. ^{b}Taken from ref 23. ^{c}Taken from ref 24. ^{d}From the National Bureau of Standards Tables of Chemical Thermodynamics Properties. *J. Phys. Chem. Ref. Data* **1982**, *11*, Suppl. No. 2. ^{e}From this work; see text. ΔH_a(acac$^•$) is estimated by the value of $\Delta G°_a$. ^{f}Taken from: Irving, R. J.; Wadso, I. *Acta Chem. Scand.* **1970**, *24*, 589. ^{g}Taken from: Hacking, J. M.; Pilcher, G. *J. Chem. Thermodyn.* **1979**, *11*, 1015. ^{h}Taken from ref 27 (see Appendix).

Throughout this report we adopt the stationary electron convention[19] which assigns a heat capacity and an entropy of 0 to the free electron. Under this convention the values of $\Delta H°_a$ for monoatomic ions at 0 K apply at all temperatures, since the heat capacities of M^{3+}(g) and M^{2+}(g) are always essentially equal. Therefore, values of $\Delta H°_a(M^{3+}$,g) are given by the negative value of the third ionization potential for the metal. The stationary electron convention is adopted to maintain consistency with the original $\Delta G°_a$ values quoted for the organic reference compounds[3] on which the results presented in this work are based.

From cycle 2 of Scheme III, $\Delta G°_a$(M(acac)$_3$,g) data can be compared with $\Delta G°_a$ for the same process in solution to yield the difference between the solvation free energies of a M(acac)$_3$ neutral and its anion. Values of $\Delta G°_a$(M(acac)$_3$,soln) can be estimated from electrochemical $E_{1/2}$ values for M(acac)$_3^{0/-}$ couples (see discussion below). Assuming $\Delta G°_a$(M(acac)$_3$,g) data at 350 K are valid at other temperatures again introduces an approximation, but using the upper limit of ~20 eu for $\Delta S°_a$, the error introduced in quoting values of $\Delta\Delta G°_{solv}$(M(acac)$_3^{0/-}$) at 298 K is again typically <1 kcal mol^{-1}.

In the thermochemical cycle used in this work to obtain values for the bond disruption enthalpies for M(acac)$_3$ and M(acac)$_3^-$ complexes, a value for $\Delta H°_a$ at 298 K for acac$^•$ radical is needed. The value obtained from the gas-phase studies is a free energy, but $\Delta S°_a$ is expected to be typically small as observed for other organic compounds. A predictable correction arises from the multiplicity change in the reactions studied. Since acac$^-$ and the neutral organic acceptors both have singlet ground states and acac radical and the organic anions are doublets, $T\Delta S_{elec}$ contributes −1.0 kcal mol^{-1} to the $\Delta G°_{rxn}$ values at 350 K. Thus ΔH_a(acac) is estimated as 58 ± 5 kcal mol^{-1}.

Homolytic and Heterolytic M–O Bond Enthalpies in M(acac)$_3$(g) Complexes and M(acac)$_3^-$(g) Ions. The difference in the total heterolytic or homolytic metal–ligand bond disruption enthalpies between any M(acac)$_3$ complex and its negative ion can be obtained from the relationships:

$$\Delta\Delta H°_{het}(\mathrm{M(acac)_3}^{0/-}) \equiv \Delta H°_{het}(\mathrm{M^{3+}\text{–}(acac^-)_3}) - \Delta H°_{het}(\mathrm{M^{2+}\text{–}(acac^-)_3}) = \Delta H°_a(\mathrm{M(acac)_3,g}) - \Delta H°_a(\mathrm{M^{3+},g}) \tag{1a}$$

$$\Delta\Delta H°_{hom}(\mathrm{M(acac)_3}^{0/-}) \equiv \Delta H°_{hom}(\mathrm{M\text{–}(acac)_3}) - \Delta H°_{hom}(\mathrm{M^-\text{–}(acac)_3}) = \Delta H°_a(\mathrm{M(acac)_3,g}) - \Delta H°_a(\mathrm{M,g}) \tag{1b}$$

Values for the electron attachment energies required for eq 1 are given in Table I. Before deriving the average bond disruption enthalpies for the gas-phase M(acac)$_3^-$ ions by using eq 1a and 1b, we first critically assessed the available data for the corresponding neutral bond enthalpies. Inaccurate assumptions made in the literature derivations required us to generate new experimental data and thereby revise the published enthalpies as discussed in the following.

For M(acac)$_3$ complexes $\Delta H°_{hom}$(M–(acac)$_3$) and the average homolytic metal–oxygen bond disruption enthalpy, $\Delta H°_{hom}$(M–O) = (1/6)$\Delta H°_{hom}$(M–(acac)$_3$), can be derived by using a thermochemical cycle. The relationship between the various thermochemical values for homolytic disruption is given in eq 2.

$$\Delta H°_{hom}(\mathrm{M\text{–}O}) = \tfrac{1}{6}\{3\Delta H°_f(\mathrm{Hacac,enol,l}) + 3\Delta H°_{vap}(\mathrm{Hacac,enol}) + 3\Delta H°_{hom}(\mathrm{H\text{–}acac,enol}) + \Delta H°_{sub}(\mathrm{M,cr}) - \Delta H°_f(\mathrm{M(acac)_3,cr}) - \Delta H°_{sub}(\mathrm{M(acac)_3,cr}) - 3\Delta H°_f(\mathrm{H,g})\} \tag{2}$$

In eq 2, $\Delta H°_{vap}$(Hacac,enol,l) is the enthalpy of vaporization of enolic acetylacetone, and $\Delta H°_{sub}$(M(acac)$_3$,cr) and $\Delta H°_{sub}$(M,cr) are enthalpies of sublimation of M(acac)$_3$ and the metal M, respectively. The relationship between $\Delta H°_{hom}$(M–O) and the average heterolytic metal oxygen bond disruption enthalpy, $\Delta H°_{het}$(M–O), is given in eq 3.

$$\Delta H°_{het}(\mathrm{M\text{–}O}) = \tfrac{1}{6}[6\Delta H°_{hom}(\mathrm{M\text{–}O}) + \sum_{i=1}^{3}\mathrm{IP}_i(\mathrm{M}) + 3\Delta H°_a(\mathrm{acac^•})] \tag{3}$$

The summation term in eq 3 is the sum of the first three ionization energies for the metal M. Values for $\Delta H°_f$ for M(acac)$_3$ complexes of the first transition metal series are available in the literature from the results of Wood and Jones using bomb calorimetry[20] and from the results of reaction calorimetry.[21-25] Reaction calorimetry is considered to be the more reliable method for M(acac)$_3$ compounds,[22,23a] and this technique has been applied to M(acac)$_3$ complexes of interest here for M = Cr, Mn, Fe, and Co.[23,24] Reaction calorimetry has also been used by Ribeiro Da Silva and co-workers to determine values of $\Delta H°_f$ and $\Delta H°_{hom}$(M–O) for other tris(β-diketonate) complexes,[23,24] and the application of the technique to transition metal β-diketonates has been reviewed.[25] Their work included a reappraisal of the values of $\Delta H°_f$ and $\Delta H°_{hom}$(M–O) derived from the original reaction calorimetry studies, and the values have been revised here using the latest values of the auxiliary thermochemical data required for their determination.

The two values that introduce the greatest uncertainty in derived bond enthalpies for the M(acac)$_3$ complexes are the values of the enthalpy of sublimation of the M(acac)$_3$ complex and the gas-phase homolytic bond disruption enthalpy of the O–H bond in the enol form of acetylacetone ($\Delta H°_{hom}$(H–acac,enol) in eq 2). With regard to the former, values for $\Delta H°_{sub}$(M(acac)$_3$) are difficult to measure precisely for compounds of relatively low

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(19) See: (a) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G., Eds. *Gas-Phase Ion and Neutral Thermochemistry*; American Institute of Physics: New York, 1988. (b) Rosenstock, H. M. In *Kinetics of Ion Molecule Reactions*; Ausloos, P., Ed.; Plenum: New York, 1979; p 246.

(20) Wood, J. L.; Jones, M. M. *Inorg. Chem.* **1964**, *3*, 1553.

(21) (a) Hill, J. O.; Irving, R. J. *J. Chem. Soc. A* **1967**, 1413. (b) Hill, J. O.; Irving, R. J. *J. Chem. Soc. A* **1968**, 1052. (c) Hill, J. O.; Irving, R. J. *J. Chem. Soc. A* **1968**, 3116.

(22) Cavell, K. J.; Pilcher, G. *J. Chem. Soc., Faraday Trans. 1* **1977**, *73*, 1590.

(23) (a) Ribeiro Da Silva, M. A. V.; Ferrao, M. L. C. C. H. *Can. J. Chem.* **1988**, *66*, 651. (b) Ribeiro Da Silva, M. A. V.; Ferrao, M. L. C. C. H. *J. Chem. Thermodyn.* **1987**, *19*, 645. (c) Ribeiro Da Silva, M. A. V.; Ferrao, M. L. C. C. H. *J. Chem. Thermodyn.* **1988**, *20*, 79.

(24) Ribeiro Da Silva, M. A. V.; Ferrao, M. L. C. C. H.; Magalhaes, A. M. L. *Thermochim. Acta* **1988**, *129* (2), 229.

(25) Ribeiro Da Silva, M. A. V. In *Thermochemistry and Its Applications to Chemical and Biochemical Systems*; Ribeiro Da Silva, M. A. V., Ed.; NATO ASI Series: Reidel: Dordrect, 1984; p 317.

Table III. Average Metal–Oxygen Bond Disruption Enthalpies[a] for Gas-Phase $M(acac)_3$ Complexes and $M(acac)_3^-$ Anions

M	$\Delta\Delta H^\circ_{het}$ $(M{-}(acac)_3^{0/-})$[b]	$\Delta H^\circ_{hom}(M{-}O)$ $M(acac)_3$	$\Delta H^\circ_{het}(M{-}O)$ $M(acac)_3$	$\Delta H^\circ_{het}(M{-}O)$ $M(acac)_3^-$	$\Delta H^\circ_{hom}(M{-}O)$ $M(acac)_3^-$
V	651				
Cr	694	45 ± 3[c]	224 ± 5[d]	108 ± 8	46 ± 3[e]
Mn	717	33 ± 3[c]	222 ± 5[d]	103 ± 8	>43
Fe	663	36 ± 3[c]	217 ± 5[d]	107 ± 8	43 ± 3[e]
Co	725	33 ± 3[c]	228 ± 5[d]	107 ± 8	38 ± 4[e]
Ru	617				

[a] All values quoted are in kcal mol^{-1}. Error limits are one-sixth of the total error estimated for complete bond disruption of the ML_3 unit. [b] Value obtained from eq 1 and gas-phase electron attachment data given in Table I. [c] Value obtained from reaction calorimetry data[23,24] corrected for value of $\Delta H^\circ_{hom}(H{-}acac,g)$ (see text). [d] Value obtained using ΔH°_a of acac$^\bullet$ estimated from this work. [e] Determined from value of $\Delta H^\circ_{hom}(M{-}O)(M(acac)_3)$ using eq 1b.

volatility such as $M(acac)_3$ complexes. For example, values for ΔH°_{sub} for $Cr(acac)_3$ quoted in the literature range from 6.64 kcal mol^{-1}, used in the bomb calorimetry study of Wood and Jones,[20] to 33.8 kcal mol^{-1} obtained more recently from differential scanning calorimetry.[26] The apparent unreliability of the values of $\Delta H^\circ_{sub}(M(acac)_3)$ used in the earlier work was recognized in the reappraisal by Ribiero Da Silva and co-workers.[24] From a review of the results available in the literature,[25] the values of $\Delta H^\circ_{sub}(M(acac)_3)$ chosen by these workers were in the range of ~28–33 kcal mol^{-1}. The same values were used in this report and are given in Table II along with the other auxiliary data used in Scheme III.

No experimental values have been available for the value of $\Delta H^\circ_{hom}(H{-}acac)$, and values used previously have been estimated. The difficulty of assessing the contributions to the relative stability of acetylacetone due to intramolecular hydrogen bonding in the enol form and the effects of electronic delocalization in the acetylacetonate radical has led to estimated values ranging from 87 to 110 kcal mol^{-1}.[20,22] A value of $\Delta H^\circ_{hom}(H{-}acac,enol)$ at 298 K can be estimated from the gas-phase proton attachment enthalpy (ΔH°_{pa}) of $acac^-$ (see Appendix),[27] ΔH°_a of acac$^\bullet$, and the ionization potential of H atom.[7] The relationship is given by:

$$\Delta H^\circ_{hom}(H{-}acac) = -\Delta H_{pa}(acac^-) - IP(H,g) - \Delta H^\circ_a(acac^\bullet) \tag{4}$$

Substituting the available data from the literature and ΔH°_a for acac$^\bullet$ determined in this report (Table II) into eq 4 yields a value of $\Delta H^\circ_{hom}(H{-}acac,enol)$ of 88 ± 6 kcal mol^{-1}.

The new value for the $\Delta H^\circ_{hom}(H{-}acac,enol)$ combined with the reaction calorimetry data leads to new values of $\Delta H^\circ_{hom}(M{-}O)$ and $\Delta H^\circ_{het}(M{-}O)$ for the $M(acac)_3$ complexes of Cr, Mn, Fe, and Co; these values are given in Table III. The homolytic M–O bond disruption enthalpies are 6 kcal mol^{-1} lower than those reported earlier based on reaction calorimetry data[23-25] as a result of the use of a lower H–acac bond enthalpy. Also given in Table III are the values of $\Delta\Delta H^\circ_{het}(M(acac)_3^{0/-})$, obtained from eq 1a and the data in Table I. The resulting $\Delta H^\circ_{het}(M{-}O)$ and $\Delta H^\circ_{hom}(M{-}O)$ values from eq 1a and 1b for the $M(acac)_3^-$ anions are listed in Table III. Note that the error limits given in Table III are one-sixth of the errors estimated for the complete homolytic and heterolytic bond disruption enthalpies of eq 1a and 1b.

The results for the average M–O heterolytic bond energies obtained in this report (Table III) are shown graphically in Figure 1. The heterolytic bond disruption enthalpies for the M(III) neutral complexes are approximately twice the values of those for the M(II) anions. Interestingly, this approximate factor of 2 is also found in comparing the heats of hydration of M^{3+} and M^{2+} ions[29] as well as the mean heterolytic bond disruption enthalpies of the M(III) metallocenium ions and M(II) metallocenes, $[Cp_2M]^+(g)$ and $Cp_2M(g)$.[2b] On the basis of these limited comparisons, the ratio of average heterolytic bond energies for these types of M(III) and M(II) complexes seems to be associated more with the formal oxidation states of the metals than with the charges on the complexes or the natures of the ligands.

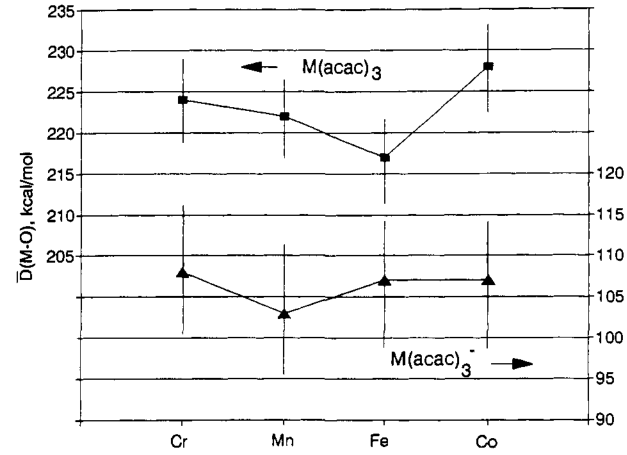

Figure 1. Average heterolytic M–O bond energies for $M(acac)_3$ complexes (upper plot) and $M(acac)_3^-$ ions (lower plot) derived in this work. Estimated error limits are shown.

The results in Table III indicate that the mean homolytic bond disruption enthalpies for the metal(II) anions are in all cases equal to or *higher* than the values for the metal(III) complexes. Thermochemically, this result can be traced to the higher electron affinities of the neutral complexes compared to the free metal atoms (Table I). The trends in homolytic bond energies for metal complexes will generally be less intuitive than found for organic compounds because significant electronic rearrangements can occur upon bond formation in the metal complexes. As expected, heterolytic energies follow a far more predictable trend when the metal oxidation state is varied.

The new values of $\Delta H^\circ_{het}(M{-}O)$ (Table III, Figure 1) are lower than those derived from bomb calorimetry results[20] because of the lower value used for $\Delta H^\circ_{hom}(H{-}acac,enol)$ and a more exothermic value for ΔH°_a(acac$^\bullet$) (a value of −34 kcal mol^{-1} was used previously). The calculated values using the bomb calorimetry results[20] provided an illustration of the formation of a part of the classic double periodic variation.[29] This trend is generally observed for heterolytic bond energies for M^{3+} and M^{2+} complex ions of the first transition metal series.[29] A relative minimum is predicted for the neutral complex with the d^5 configuration (M = Fe) for which the ligand field stabilization energy is zero.[29] An analogous rationale applies to the trend observed for the $M(acac)_3^-$ anions, where the d^5 configuration for $M(acac)_3^-$ anions occurs for Mn and a minimum value is again predicted. The average ΔH°_{het} values (Figure 1) follow the predicted trend; however, the derived heterolytic bond disruption enthalpies in this work are all equal within the estimated errors for the $M(acac)_3$ and $M(acac)_3^-$ series (Table III), so no firm conclusions about the presence of such a trend in the gas-phase results can be drawn.

Relative Solvation Energies of $M(acac)_3(g)$ and $M(acac)_3^-(g)$. The difference in ΔG°_{solv} values between a $M(acac)_3$ complex and its anion ($\Delta\Delta G^\circ_{solv}(M(acac)_3^{0/-})$)[30] is defined here by eq 5 and

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(26) Murray, J. P.; Hill, J. O. *Thermochim. Acta* **1984**, *72* (3), 341.
(27) Cumming, J. B.; Kebarle, P. *Can. J. Chem.* **1978**, *56*, 1.
(28) Benson, S. W.; O'Neil, H. E. *Nat. Stand. Bur. Stand.* **1970**, *No. 21*.
(29) (a) McClure, D. S. In *Some Aspects of Crystal Field Theory*; Dunn, T. M., McClure, T. M., Pearson, R. G., Eds.; Harper and Row: New York, 1965. (b) Figgis, B. N. *Introduction to Ligand Fields*; Interscience: New York, 1966; Chapter 5. (c) Burdett, J. K. *Molecular Shapes*; Wiley-Interscience: New York, 1980; Chapter 10.

applies to the reaction in eq 6.

$$\Delta\Delta G^\circ_{\text{solv}}(\text{M(acac)}_3{}^{0/-}) = \Delta G^\circ_{\text{solv}}(\text{M(acac)}_3{}^-) - \Delta G^\circ_{\text{solv}}(\text{M(acac)}_3) \quad (5)$$

$$\text{M(acac)}_3\text{(soln)} + \text{M(acac)}_3{}^-\text{(g)} \rightarrow \text{M(acac)}_3\text{(g)} + \text{M(acac)}_3{}^-\text{(soln)} \quad (6)$$

Thermodynamic data for reversible electron attachment to electroactive species in solution are normally given as standard electrode potentials (E° values), measured relative to the standard hydrogen electrode (SHE). For many species these data can be conveniently estimated from $E_{1/2}$ values, measured against a reference electrode, by using, for example, polarography or cyclic voltammetry. In order to directly compare $E_{1/2}$ data obtained for $\text{M(acac)}_3{}^{0/-}$ couples to the corresponding gas-phase $\Delta G^\circ_{\text{a}}$ values, the zero of potential for the "free" electron in reactions b and c of State III must be set to the same reference state. Defining "absolute" magnitudes of electron attachment energies in solution requires that the potential of the reference electrode be redefined on this absolute scale (to yield an E°_{abs}(ref) value). The absolute electron attachment energy for M(acac)_3 complexes in solution ($\Delta G^\circ_{\text{a}}(\text{M(acac)}_3\text{,soln})$ is then estimated by eq 7, where F is the Faraday constant.

$$\Delta G^\circ_{\text{a}}(\text{M(acac)}_3\text{,soln})) = -F\{E_{1/2}(\text{M(acac)}_3{}^{0/-}) + E^\circ_{\text{abs}}(\text{ref})\} \quad (7)$$

With a value for $\Delta G^\circ_{\text{a}}(\text{M(acac)}_3\text{,soln})$, a value for $\Delta\Delta G^\circ_{\text{solv}}(\text{M(acac)}_3{}^{0/-})$ can be obtained from eq 8, as illustrated by cycle 2 in Scheme III.

$$\Delta\Delta G^\circ_{\text{solv}}(\text{M(acac)}_3{}^{0/-}) = \Delta G^\circ_{\text{a}}(\text{M(acac)}_3\text{,soln}) - \Delta G^\circ_{\text{a}}(\text{M(acac)}_3\text{,g}) \quad (8)$$

The absolute value of the electrochemical potential of a galvanic half-cell is thermodynamically related to single ion solvation energies. Although *relative* single ion solvation energies are readily obtainable from Born cycles and emf measurements, the *absolute* contribution from *each* ion to the solvation energy of ± ion pairs is difficult to evaluate. There have been attempts to estimate the absolute value of the enthalpy and free energy of hydration of the proton.[31-38] A variety of different methods have been used, which have been categorized by Haliwell and Nyburg,[34] and the various methods that have led to literature values for the thermodynamics of H^+ solvation have been critically reviewed by Conway.[39] A recent value for the free energy of hydration of the proton of -260.0 ± 0.5 kcal mol^{-1} has been provided by Farrell and McTigue,[37] based on measurements of volta potential differences. This method has the advantage that it provides the most direct method for the determination of "real" free energies of solvation of ions, and intrinsically includes the work required to pass a charge across the surface potential ($\Delta\chi$) that exists at the surface of liquids. This work is not included in the values of $\Delta H^\circ_{\text{solv}}$ or $\Delta G^\circ_{\text{solv}}$ obtained by applying "physical model" approaches,[34,39] and such values are termed "chemical" free energies of solvation. A drawback of the volta potential method is that the reference state of the electron is stationary at a point in a vacuum close to the surface of the solution, under the influence of the volta potential of the solution (Ψ^s). As shown by Trasatti,[40] an amount of work equal to $zF\Psi^s$ must be done to move the electron away to field free space (the reference state used to define single ion solvation energies in accord with the stationary electron convention). The magnitude of this work is uncertain. As no experimental procedure has directly led to the single ion solvation free energy of the proton with the necessary free electron reference state, one is left with choosing a value based on a method for which the assumptions and principles are the least unsatisfactory.

Table IV. Polarographic Data and Differential Solvation Free Energies for $\text{M(acac)}_3{}^{0/-}$ Complexes

$\text{M(acac)}_3{}^{0/-}$ couple	$E_{1/2}{}^a$	$\Delta G^\circ_{\text{a}}(\text{M(acac)}_3\text{,solv})^b$	$\Delta\Delta G^\circ_{\text{solv}}(\text{M(acac)}_3{}^{0/-})^b$
		Acetonitrile	
Cr	-1.81^c	-66.3	-46
Ru	-0.70^d	-91.3	-52
Fe	-0.67^c	-92.6	-50
Co	-0.34^e	-100.0	-53
Mn	-0.09^f	-111	-52
		Dimethyl Sulfoxide	
V	-1.42^g	-75.2	-50
		Dichloromethane	
Ru	-0.71^d	-91.1	-52
		Water	
Ru	-0.51^h	-96.2	-58

[a] Values given in volts measured using 0.1 M TEAP as supporting electrolyte against SCE, except Ru(acac)_3 in acn (n-BuNBF_4 versus Ag/AgCl) and in water (see ref 50 for details). [b] Values given in kcal mol^{-1}, obtained from eq 7 and 8. [c] Murray, R. W.; Hiller, L. K. *Anal. Chem.* **1967**, *39*, 1221. [d] Tocher, J. H.; Fackler, J. P. *Inorg. Chim. Acta* **1985**, *102*, 211. [e] Tsiamis, C.; Cambanis, S.; Hadjikostas, C. *Inorg. Chem.* **1987**, *26*, 26. [f] Yamaguchi, K.; Sawyer, D. T. *Inorg. Chem.* **1985**, *24*, 971. [g] Mohd, A. N.; Riechel, T. L. *Inorg. Chem.* **1981**, *20*, 1974. [h] Reference 50.

The value of $\Delta G^\circ_{\text{hyd}}(H^+)$ quoted by Farrell and McTigue is in good agreement with an earlier determination by the same method by Randles,[32] and is not dissimilar to estimated values based on physical models.[31,33-35] This value has been used by Kebarle[41] and by Shalev and Evans[42] in a cycle similar to cycle 2 in Scheme III to determine the solvation energies of a variety of quinones and nitrobenzenes. Adopting the recommended value[39] for $\Delta G^\circ_{\text{hyd}}(H^+)$ allows the absolute potential of the standard hydrogen electrode to be evaluated,[40,43] and a value of -102.6 kcal mol^{-1} (4.44 V) is obtained as the absolute potential for the SHE. Values for E°_{abs}(ref) based on this scale are used with $E_{1/2}$ data in eq 7 and 8 to obtain values for $\Delta G^\circ_{\text{a}}(\text{M(acac)}_3\text{,soln})$ and $\Delta\Delta G^\circ_{\text{solv}}(\text{M(acac)}_3{}^{0/-})$.

Polarographic data are given in Table IV for the reversible electrochemical reduction of several M(acac)_3 complexes in acetonitrile cited from various literature sources. To facilitate comparison, data are quoted wherever possible from results obtained under common electrochemical conditions (acetonitrile with 0.1 M tetraethylammonium perchlorate as supporting electrolyte). For V(acac)_3, however, $E_{1/2}$ data are only available for dimethyl sulfoxide (DMSO) as the solvent. To allow a comparison of solvation free energies in different solvents, data for the reduction of Ru(acac)_3 in dichloromethane and water are included. The $E_{1/2}$ data lead to values of $\Delta G^\circ_{\text{a}}(\text{M(acac)}_3\text{,soln})$ and $\Delta\Delta G^\circ_{\text{solv}}(\text{M(acac)}_3{}^{0/-})$, which are also included in Table IV. The accuracies of these values are difficult to assess since they rely on the value chosen for the single ion solvation energy of the proton and the approximation of $E_{1/2}$ to true E° values. Unfortunately, because of the low solubility of M(acac)_3 complexes in water, the latter approximation is made worse for the majority of the data in Table IV, since the $E_{1/2}$ values quoted are measured in nonaqueous solvents against an aqueous reference electrode. Consequently,

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(30) The quantity $\Delta\Delta G^\circ_{\text{solv}}(\text{M(acac)}_3{}^{0/-})$ represents the free energy change occurring in the redox couple $\text{M(acac)}_3{}^{0/-}$ and not the quantity $\Delta G^\circ_{\text{solv}}(\text{M(acac)}_3{}^0) - \Delta G^\circ_{\text{solv}}(\text{M(acac)}_3{}^-)$, which has the opposite sign.

(31) Latimer, W. M.; Pitzer, K. S.; Slansky, C. M. *J. Chem. Phys.* **1939**, *7*, 108.

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(43) Bard, A. J., Parsons, R., Jordon, J., Eds. *Standard Potentials in Aqueous Solution*; Marcel Dekker: New York, 1985.

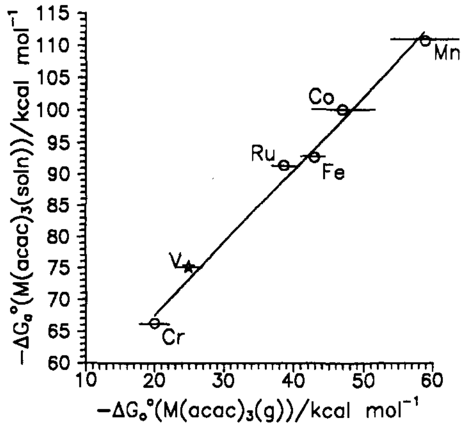

Figure 2. Plot of electron attachment free energies for M(acac)$_3$ complexes in the gas-phase versus the estimated values in acetonitrile. The electron attachment energy for V(acac)$_3$ in the gas-phase versus in DMSO is also shown. Estimated error limits on gas-phase energies are shown.

any junction potential that exists at the solvent/reference electrode interface will be included in the observed $E_{1/2}$ values. This problem was minimized by Shalev and Evans[42] in obtaining $\Delta\Delta G°_{\text{solv}}$ values for organic compounds by including a cobaltocenium/cobaltocene internal standard. The absolute standard potential of this Cp_2Co couple was assumed to be largely solvent independent as is assumed for the $Cp_2Fe^{+/0}$ couple, but this latter assumption is known to be somewhat unsatisfactory because of different solvent ordering effects for various polar solvents.[44] The value of $\Delta\Delta G°_{\text{solv}}(\text{Ru(acac)}_3{}^{0/-})$ obtained in water, however, may be considered to be a reasonable estimate since junction potentials are minimized and $E_{1/2}$ will closely approximate $E°$.

Figure 2 shows a plot of gas-phase $\Delta G°_a(\text{M(acac)}_3,\text{g})$ values versus $\Delta G°_a(\text{M(acac)}_3,\text{soln})$ values in acetonitrile for the M(acac)$_3$ complexes for which data are available (Tables I and IV). The value for V(acac)$_3$ is also shown since $E_{1/2}$ values for M(acac)$_3$ complexes in DMSO are typically similar to those in acetonitrile, generally being some ≤ 100 mV or so more positive. As can be seen, there is a strong linear correlation between the two data sets. The best fit line has unit slope within estimated errors, indicating that differential solvation energies for M(acac)$_3{}^{0/-}$ couples are essentially constant (Table IV). It should be noted that this conclusion is independent of the choice of the absolute electrode potential. The same data are presented in Figure 3 as a periodic trend to illustrate the relative magnitudes of electron attachment energies in the gas-phase and in solution.

It is interesting to compare the experimental values of $\Delta\Delta G°_{\text{solv}}(\text{M(acac)}_3{}^{0/-})$ in Table IV to the values predicted from dielectric continuum theory. The Born equation[45] predicts the change in electrostatic free energy $\Delta G°_{\text{el}}$ when a charge is transferred from a conducting sphere of effective (thermochemical) radius r_{eff} in a vacuum, to a sphere of equal radius in a medium of dielectric constant D. A convenient form of the equation for ions in solution is given in eq 9,

$$\Delta G°_{\text{el}} = -(166z^2/r_{\text{eff}})(1 - 1/D) \text{ kcal mol}^{-1} \qquad (9)$$

where z is the integral units of electronic charge and D is the dielectric constant of the solvent. It can be seen from the above definition that the Born equation applies to the process in eq 6, and therefore $\Delta G°_{\text{el}}$ can be related directly to $\Delta\Delta G°_{\text{solv}}$(note that a correction for change in standard state need not be applied for eq 6 since gas and solution states cancel). The Born equation is compared to "chemical" single ion free energies of solvation, since the work of transferring an ion across the surface of the solvent is not considered. The additional work is probably small, however, when compared with typical values of $\Delta\Delta G°_{\text{solv}}$,[40] and so useful comparisons may still be made to the $\Delta\Delta G°_{\text{solv}}(\text{M(acac)}_3{}^{0/-})$ values obtained in this work.

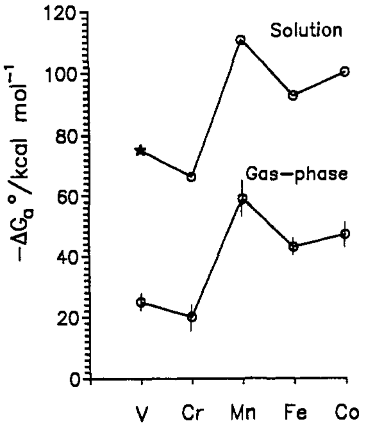

Figure 3. Plot showing periodic trends of electron attachment energies in the gas-phase and in solution. Solution-phase data are for acetonitrile (circles) and DMSO (star). Estimated error limits on gas-phase energies are shown.

Using the value of $\Delta\Delta G°_{\text{solv}}(\text{Ru(acac)}_3{}^{0/-})$ of 57.5 kcal mol^{-1} in water, the Born equation gives a value of r_{eff} of 2.9 Å, while the maximum radius for Ru(acac)$_3{}^{0/-}$ is expected to be ~6 Å, the maximum radius of Ru(acac)$_3$.[46] The smaller Born thermochemical radius, compared to the crystallographic radius, is not unexpected since the molecular shapes and charge distributions in the M(acac)$_3{}^{0/-}$ couple are poorly approximated by neutral and charged spheres. The tris chelate coordination environment can allow the first solvation layer to penetrate the ~6 Å sphere based on the distance between metal center and methyl hydrogens. The relative extents to which solvent penetration and specific solvation of the polar metal–ligand interactions influence the solvation energies cannot be deduced from the present results. It is notable that the deduced $\Delta\Delta G°_{\text{solv}}(\text{Ru(acac)}_3{}^{0/-})$ values for dichloromethane and acetonitrile solvents are 6 kcal mol^{-1} lower than the value for water. Given the approximations inherent in the method used, however, this magnitude of difference could arise from either actual variations in solvation free energies for the nonaqueous versus water solvents or errors introduced by the electrochemical potential determinations.

The vertical ionization energies of several ruthenium tris(β-diketonates) have been combined with polarographic data by other workers to obtain information about relative solvation energies.[47] For these Ru compounds, the ionization is from a metal-based approximately nonbonding orbital, and the PES data can be justifiably used in place of the adiabatic values with relatively small errors.

Conclusions

The availability of free energies of electron attachment for a series of gas-phase metal tris(acetylacetonate) complexes has allowed the first systematic thermochemical evaluation of average bond disruption enthalpies as a function of metal and oxidation state in gas-phase coordination complex ions. The thermal electron-transfer gas-phase equilibrium method yields free energies of electron attachment (or ionization) that can be directly incorporated into thermochemical cycles. Other methods of determining such energies, such as photoelectron spectroscopy, are less generally useful since transition metal complexes often undergo large geometry changes upon oxidation or reduction that can lead to erroneous estimates of thermal electron attachment or ionization energies.

In addition, when combined with solution electrochemical data, the $\Delta G°_a$ values for the gas-phase neutral complexes have led to the most extensive evaluation to date of differential solvation

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[44] Sahami, S.; Weaver, M. J. *J. Solution Chem.* **1981**, *10*, 199.

[45] (a) Born, M. *Z. Phys.* **1920**, *1*, 45. (b) For a concise review of Born models applied to solvation, see: Gomez-Jeria, J. S.; Morales-Lagos, D. *J. Phys. Chem.* **1990**, *94*, 3790.

[46] Kung-Jou Chao, G.; Sime, R. L.; Sime, R. J. *Acta Crystallogr.* **1973**, *B29*, 2845.

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energies, $\Delta\Delta G^\circ_{solv}$, for transition metal complex redox couples. In contrast to the results for the metallocene/metallocenium couples reported elsewhere,[2b,48] the Born charging model does not provide a reasonable estimate of the differential solvation free energy for the tris chelate complexes studied here. Although the inadequacy of the Born model combined with crystallographic radii for predicting solvation free-energy changes for redox processes for many transition metal complexes has been suggested in other contexts (e.g., in attempted fits of optical electron-transfer phenomena using the dielectric continuum model[49]), direct thermochemical evaluation of these effects has been lacking until this study. The $\Delta\Delta G^\circ_{solv}$ values can be used in principle to derive single ion solvation free energies for complex ions if the free energy of solvation for the neutral complex is available.

In considering the data in Tables I, III, and IV, it is striking to note how greatly the range and magnitude of the electron attachment energies for the free $M^{3+}(g)$ ions (29.3–33.7 eV) are diminished in the corresponding $M(acac)_3$ complexes (0.9–2.6 eV). Solvation of a gas-phase $M(acac)_3$ complex increases the electron attachment energy by a relatively constant amount ($\sim$2.2 V for acetonitrile as the solvent). The role of solvation is therefore somewhat secondary to that of ligation (cycle 1 in Scheme III) in determining the magnitude of the electrode potential for a particular $M(acac)_3^{0/-}$ redox couple. However, when considered on the scale of typical free-energy changes for homogeneous redox reactions of transition metal complexes, changes in solvation energies in reactants and products clearly can have a profound influence on the reaction thermodynamics. As more gas-phase data become available, a more complete quantitative understanding of solvation and bond energies in coordination chemistry will certainly result.

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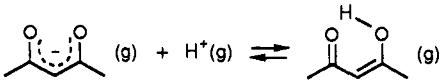
Appendix

The application of eq 4 to estimate the value of ΔH°_{hom}(H-acac,enol) assumes that the enthalpy of proton attachment given by Cumming and Kebarle[27] ($\Delta H^\circ_{pa} = -344$ kcal mol^{-1} at 300 K) is valid for the equilibria involving only the *enol* form of Hacac (eq A1). The analysis of the thermochemistry for eq A1 is



(A1)

complicated by the well-known enol–keto equilibrium associated with the Hacac neutral. Melia and Merrifield[51] give the following values for the enol = keto equilibrium in the gas phase: $\Delta H^\circ_{e-k} = 2.13 \pm 0.20$ kcal mol^{-1}, $\Delta S^\circ_{e-k} = 1.7 \pm 0.5$ cal mol^{-1} deg^{-1}. Thus, the enol form is preferred enthalpically, but increasing temperature favors the keto form via the entropy term.[52] At 298 K, these thermodynamic values yield 94% enol form for an Hacac sample, while at 600 K the mixture is $\sim$70% enol (assuming the parameters are roughly transferable to the higher temperature, as suggested by the low-entropy change and the small change in heat capacities). Thus, the ΔH°_{pa} value given for acac$^-$ by Cumming and Kebarle[27] was derived from data for a mixture of the enol and keto forms present in the mass spectrometer source at 600 K. The estimate of the acac$^-$ proton affinity[27] was evidently based on the assumption that only the keto form was present. The enol/keto equilibrium therefore will contribute to errors in the estimation of the H–acac(enol) bond disruption enthalpy from proton affinity data.

It is possible to estimate the magnitude of the error resulting from the use of $\Delta H^\circ_{pa} = -344$ kcal mol^{-1} in eq 4. The following analysis assumes that the anion acac$^-$ has a unique structure in the range of 298–600 K. Cumming and Kebarle[27] have estimated $\Delta S^\circ = 4.7$ cal deg^{-1} mol^{-1} for:

$$\text{acac}^-(\text{g},600\text{K}) = \text{Hacac}(\text{keto},\text{g},600\ \text{K}) \qquad \text{(A2)}$$

We have repeated the statistical calculation of ΔS° (eq A2) and estimate a value of 4.0 cal deg^{-1} mol^{-1}.[53]

Cumming and Kebarle[27] determined the free-energy change for ea A3 at 600 K to be 7.8 kcal mol^{-1}.

$$\text{Cl}^- + \text{Hacac}(\text{enol/keto mixture}) = \text{HCl} + \text{acac}^- \qquad \text{(A3)}$$

Assuming the thermodynamic values quoted above for the enol/keto equilibrium are approximately valid at 600 K, eq A4 is readily obtained.

$$\Delta G^\circ_{obsd}(\text{eq A3},600\ \text{K}) = 7.8\ \text{kcal mol}^{-1} = 0.7\ (\Delta G^\circ(\text{enol})) + 0.3\ (\Delta G^\circ(\text{keto})) \qquad \text{(A4)}$$

The free-energy terms on the right side of eq A4 are the contributions of the enol and keto forms to the total free-energy change. From the estimated free-energy difference between the enol and keto forms at 600 K (1.1 kcal mol^{-1}), a value of $\Delta G^\circ(\text{keto}) = 7.0$ kcal mol^{-1} is obtained. The enthalpy change at 600 K for ea A3 is then obtained as 10.2 kcal mol^{-1} by using the estimated ΔS° value[53] for acac$^-$ → Hacac(keto) along with the Cl$^-$/HCl ΔS° value (9.4 eu). The same rotational and vibrational parameters used in the entropy calculations[53] are used to estimate the heat capacity difference between acac$^-$ and Hacac(keto) and thereby ΔH°(eq A5,298 K) is estimated as 9.5 kcal mol^{-1}.

$$\text{Cl}^- + \text{Hacac}(\text{keto}) = \text{HCl} + \text{acac}^- \qquad \text{(A5)}$$

From the known proton attachment enthalpy for Cl$^-$ (-333.4 kcal mol^{-1}) and the enthalpy difference for the enol/keto equilibrium,[51] an estimate of $\Delta H^\circ(\text{eq A1}) = -345$ kcal mol^{-1} is obtained. These calculations indicate the magnitude of error expected in applying the proton affinity values of acac$^-$ derived from experiments using a mixture of the enol and keto forms. Combining the error limits suggested by Cumming and Kebarle[27] for their ΔH°_{pa}(300 K) values ($\pm$ 2 kcal mol^{-1}) and an additional $\pm$1 kcal mol^{-1} to account for the uncertainty due to the enol/keto equilibrium, a value of -344 ± 3 kcal mol^{-1} is suggested for the value of ΔH°_{pa}(eq A1,298 K).

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(52) The keto form presumably has greater internal rotational entropy than the enol, which has an intramolecular H bond. However, statistical mechanical estimates show that the relatively small value of the entropy change for the enol = keto equilibrium is not explicable in terms of internal rotations alone. For example, the keto form is disfavored entropically by its higher rotational symmetry number (2 versus 1 for the enol) and the higher bending vibrational frequencies of the keto sp^3 CH$_2$ group compared to the sp^2 C–H and O–H groups in the enol.

(53) The statistical mechanical calculations were carried out for model structures generated via the Sybyl molecular mechanics program (Tripos) to provide the coordinates for calculation of the external rotational moments and the reduced moments for the relevant internal rotations. The internal barriers estimated in ref 27 were used. The reduced internal rotation barriers in the keto form contribute an estimated 3.7 eu to eq A2. Vibrational entropy changes were estimated from the frequency changes that occur upon protonation of the anion. Although two C–H bends and a stretch are gained upon protonation of acac$^-$, the bending frequencies also increase in going from an sp^2 central carbon to sp^3 in the ketone. Frequencies for acac$^-$ and Hacac(keto) were estimated by reference to metal(acac$^-$)$_n$ complexes[54] and the assigned frequencies for the methylene modes of propane,[55] respectively. The somewhat lower ΔS° value estimated here (4.0 eu) compared to that in ref 27 (4.7 eu) apparently arises from the incorporation of the changes in these bending frequencies. However, it should be noted that these entropy estimates may be in error by substantially more the 0.7-eu difference noted.

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