Thermodynamics of Association of Tris(acetylacetonato)chromium(III) and -cobalt(III) with 3,5-Dichlorophenol through Hydrogen Bonding

Shoichi KATSUTA and Nobuo SUZUKI*
Department of Chemistry, Faculty of Science, Tohoku University, Sendai 980
(Received August 27, 1992)

Synopsis. The association constants of tris(acetylacetonato)chromium(III) and -cobalt(III) with 3,5-dichlorophenol in heptane were determined by a liquid-liquid partition technique at 287.7—308.2 K; the association enthalpies and entropies were calculated. The obtained enthalpies indicate considerably strong hydrogen bonds between these chelates and the phenol.

The specific interactions of neutral metal chelates with organic molecules can play an important role in the solvent extraction of the metal chelates. Especially, the adduct formation via coordination of organic bases to coordinatively unsaturated metal chelates has been well studied in connection with the synergistic effect in extraction.[1] On the other hand, the importance of hydrogen bonding in the chelate extraction was first manifested in our recent studies: Halogenated phenols were found to greatly enhance the extraction of metal acetylacetonates[2—7] and 8-quinolinolates[8] by forming hydrogen-bonded complexes with the chelates in the organic phase. Such hydrogen bonding of phenols to chelates has so far been little studied, and no thermodynamical information is available. In this paper, the thermodynamic functions for the association of coordinatively saturated tris(acetylacetonato)chromium(III) ($[Cr(acac)_3]$) and -cobalt(III) ($[Co(acac)_3]$) with 3,5-dichlorophenol (DCP) in heptane are evalulated using a liquid-liquid partition technique.

Theoretical

The apparent partition coefficient (P'_M) of a metal(III) acetylacetonate ($[M(acac)_3]$) between the heptane (org) and aqueous (aq) phases in the presence of DCP can be expressed as follows:[2—4]

$$P'_M = P_M \left(1 + \sum_{i=1}^{n} \beta_{ass,i} [DCP]_{org}{}^{i}\right), \quad (1)$$

where P_M denotes the intrinsic partition coefficient of $[M(acac)_3]$, defined as $[[M(acac)_3]]_{org}/[[M(acac)_3]]_{aq}$; $\beta_{ass,i}$ is the overall association constant in the organic phase,

$$\beta_{ass,i} = \frac{[[M(acac)_3]\cdot i DCP]_{org}}{[[M(acac)_3]]_{org}[DCP]_{org}{}^{i}}. \quad (2)$$

Therefore, the following equation is derived:

$$P'_M/P_M = 1 + \sum_{i=1}^{n} \beta_{ass,i} [DCP]_{org}{}^{i}. \quad (3)$$

The association constant can be determined by analyzing the log (P'_M/P_M) vs. log $[DCP]_{org}$ plot. The equilibrium concentration of DCP in the organic phase, $[DCP]_{org}$, is evaluated from the following equation when the amount of DCP associated with $[M(acac)_3]$ is negligibly small against the total amount of DCP:

$$[DCP]_{org} = C_{DCP} \Big/ \left(V_{aq} V_{org}{}^{-1} P_{DCP}{}^{-1} + 1\right), \quad (4)$$

where C_{DCP} denotes the initial concentration of DCP, and P_{DCP} is the partition coefficient of DCP, defined as $[DCP]_{org}/[DCP]_{aq}$. V_{aq} and V_{org} are the volumes of the aqueous and organic phases, respectively.

The standard enthalpy of the association is expressed as follows based on the van't Hoff equation:

$$\Delta H^\circ = -R[\partial \ln \beta_{ass,i} / \partial(1/T)]. \quad (5)$$

If ΔH° is almost constant within the temperature range investigated, the plot of $R \ln \beta_{ass,i}$ vs. $1/T$ should give a straight line with a slope of ΔH°. The standard free energy and entropy are given as

$$\Delta G^\circ = -RT \ln \beta_{ass,i} \quad (6)$$

and

$$\Delta S^\circ = (1/T)(\Delta H^\circ - \Delta G^\circ). \quad (7)$$

The standard state of these thermodynamic functions corresponds to unit mol dm^{-3} in heptane.

Experimental

The chemicals used were purified as described previously.[3,4] An aqueous solution (0.10 mol dm^{-3} sodium perchlorate, 5 cm^3) containing 1.9×10^{-5}—2.9×10^{-4} mol dm^{-3} $[Cr(acac)_3]$ or $[Co(acac)_3]$ was equilibrated with pure heptane or a heptane solution (1—5 cm^3) containing 2.0×10^{-4}—1.3×10^{-2} mol dm^{-3} DCP by stirring for 30 min in a thermostat at 287.7—308.2 K. The partition coefficient of each chelate in the absence (P_M) or presence (P'_M) of DCP was determined by a spectrophotometric determination of the chelate in the aqueous phase.[2—4] The partition coefficient of DCP (P_{DCP}) was also determined by a similar batch technique.

Results and Discussion

The P_M of each chelate was measured more than four times at different chelate concentrations in the range 2.8×10^{-5}—2.6×10^{-4} mol dm^{-3}. The P_{DCP} was also measured four times at different DCP concentrations, 2.1×10^{-4}—2.9×10^{-2} mol dm^{-3}. Both of the partition coefficients were confirmed to be constant regardless of

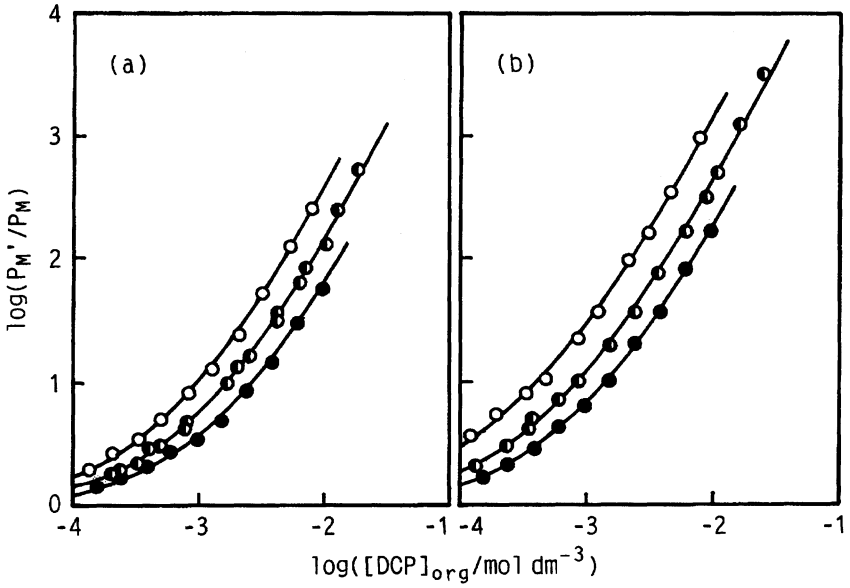

Fig. 1. Enhancement of the partition coefficient of $[Cr(acac)_3]$ (a) and $[Co(acac)_3]$ (b) as a function of the equilibrium concentration of DCP in the organic phase. ○: 287.7 K, ◐: 298.2 K, ●: 308.2 K. The data at 298.2 K are cited from our previous studies.[3,4]

the concentrations of the partitioning solutes. The averages and standard deviations of the P_M and P_{DCP} values at 287.7—308.2 K are listed in Table 1. The thermodynamics of the liquid-liquid partition of metal acetylacetonates[10,11] and phenols[12] has been described by other authors.

Figure 1 shows the plots of $\log (P'_M/P_M)$ vs. $\log [DCP]_{org}$ at different temperatures. The total amount of the chelates was always adjusted so as to be sufficiently small compared to that of DCP, so that $[DCP]_{org}$ could be calculated from Eq. 4 using the P_{DCP} value at the corresponding temperature. The partition coefficients of both the chelates rise rapidly with an increase in $[DCP]_{org}$ and the slopes of the plots become close to two in the higher concentration region of DCP at any temperature. This means that two molecules of DCP can associate with one molecule of the chelates. From these plots, the association constants were computed by a non-linear least-squares method on the basis of Eq. 3; they are listed in Table 2. The obtained association constants increase with decreasing temperature.

Each plot of $R\ln \beta_{ass,i}$ (i=1, 2) vs. $1/T$ gave a good linear relation with a correlation coefficient of more than 0.998. The standard enthalpies of the association were determined as the slopes of the plots by a linear least-squares method. The standard free energies and entropies were calculated from Eqs. 6 and 7, respectively. The obtained thermodynamic functions at 298.2 K are summarized in Table 3.

The negative values of $\Delta H°$ and $\Delta S°$ obviously reflect the exothermic bond formation between the chelate and phenol molecules and the concomitant decrease in the degree of freedom of the molecules, respectively. Although the organic phase is saturated with water (the solubility of water in heptane at 298.2 K is 3.4×10^{-3} mol dm^{-3}), our determinations of the water content in the organic phase by Karl Fisher titrations showed that

Table 1. Partition Coefficients (P_M and P_{DCP}) of $[Cr(acac)_3]$, $[Co(acac)_3]$, and DCP between Heptane and 0.10 mol dm^{-3} Sodium Perchlorate Solution

Compound	287.7 K	298.2 K	308.2 K
$[Cr(acac)_3]$	0.198±0.012	0.370±0.018[a]	0.679±0.010
$[Co(acac)_3]$	0.040±0.002	0.095±0.005[b]	0.173±0.005
DCP	1.82±0.04	2.61±0.12[c]	2.88±0.05

a) Ref. 4. b) Ref. 3. c) Ref. 9.

Table 2. Association Constants of Tris(acetylacetonato)metal(III) with DCP in Heptane

Chelate		287.7 K	298.2 K	308.2 K
$[Cr(acac)_3]$	$\log \beta_{ass,1}$	3.80	3.56[a]	3.38
	$\log \beta_{ass,2}$	6.50	6.04[a]	5.59
$[Co(acac)_3]$	$\log \beta_{ass,1}$	4.22	3.88[b]	3.64
	$\log \beta_{ass,2}$	7.10	6.58[b]	6.16

a) Ref. 4. b) Ref. 3.

Table 3. Thermodynamic Functions for the Association of Tris(acetylacetonato)metal(III) with DCP in Heptane at 298.2 K

Association complex	$\Delta H°$ / kJ mol^{-1}	$\Delta S°$ / J K^{-1} mol^{-1}	$\Delta G°$ / kJ mol^{-1}
$[Cr(acac)_3]$·DCP	−34.9	−49.0	−20.3
$[Cr(acac)_3]$·2DCP	−75.6	−138	−34.5
$[Co(acac)_3]$·DCP	−48.2	−87.2	−22.2
$[Co(acac)_3]$·2DCP	−78.0	−135	−37.6

the phenol, chelates, and their association complexes are only slightly hydrated in the organic phase. Therefore, the effect of water on the association thermodynamics should be negligible.

The ΔH° and ΔS° terms contribute antagonistically to the ΔG° term, as judged from the relation $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$. However, the contribution of the ΔH° term is larger than that of the ΔS° term, and the ΔG° value increases with an increase in the ΔH° value. The association thermodynamics is consequently governed by the ΔH° term.

The existence of the hydrogen bond between the hydroxyl hydrogen atom of the phenol and the ligands (probably oxygen atoms) of the chelates was previously evidenced by ^{1}H NMR and UV spectroscopies.[2—4] The enthalpies for $[Co(acac)_3]$ are a little more negative than those for $[Cr(acac)_3]$, indicating the higher hydrogen-bond acceptor ability of the cobalt(III) chelate. The enthalpies of the 1 : 2 association of these chelates with DCP are about twice as much as those of the 1 : 1 association. It appears that the two hydrogen bonds in the 1 : 2 association complex are nearly equivalent and independent each other.

The enthalpies corresponding to one hydrogen bond in the association complexes are evaluated as being -30 to -50 kJ mol^{-1}. These values indicate the considerably strong hydrogen bonds between the chelates and DCP: the enthalpies reported for hydrogen bonding are generally $-(8—40)$ kJ mol^{-1}.[13] Furthermore, the enthalpies of the 1 : 2 association are negatively larger than those reported for some adduct formation systems via coordination: e.g., $\Delta H^\circ = -53$ kJ mol^{-1} for the coordination of trioctylphosphine oxide to tetrakis(thenoyltrifluoroacetonato)thorium(IV) in dry benzene.[14] Thus, the hydrogen bonding with phenols can be a very strong interaction for metal chelates in solution.

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