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The Formation and Extraction Equilibria of Several Manganese(II) β-Diketonates and Their Trioctyl-Phosphine Oxide Adducts

Tatsuya SEKINE, Ryokichi MURAI, Kazuhiko TAKAHASHI, and Shigehisa IWAHORI
Department of Chemistry, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo 162

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Synopsis. From the distribution ratio of manganese(II) between carbon tetrachloride containing various amounts of β-diketone (HA) and trioctylphosphine oxide (TOPO), and an aqueous 1 mol dm^{-3} perchlorate solution at 25 °C, the formation constants for the aqueous chelates and the TOPO adducts of the MnA_2, and the partition constants for the MnA_2 chelates were determined. The constants were then compared with those of other divalent metal ions.

Measurements have previously been made of the solvent extraction equilibria of four divalent metal ions with several β-diketones in carbon tetrachloride and also of the adduct formation equilibria of the extracted chelates with trioctylphosphine oxide (TOPO).[1-4] The present paper will report the results with manganese(II) under identical conditions and will compare the equilibrium constants thus obtained with those for the other divalent metal ions.

Experimental and Statistical

The experiments were performed at 25±0.3 °C in a manner similar to those used previously.[1-4] The initial organic phase was carbon tetrachloride containing various amounts of a certain β-diketone and TOPO, and the initial aqueous phase was a 1 mol dm^{-3} sodium perchlorate solution containing an acetate buffer (less than 0.01 mol dm^{-3}) or no buffer (when the β-diketone buffered) and 2×10^{-6} to 2×10^{-4} mol dm^{-3} of manganese(II). The two phases in a stoppered glass tube were placed on a rotating framework, agitated at 20 r.p.m., and then centrifuged. The metal content in each phase was determined by an atomic absorption method. The hydrogen-ion concentration was determined by potentiometry in stoichiometric units.

The distribution ratio was defined as

$$D = [\mathrm{Mn(II)}]_{\mathrm{org,total}}[\mathrm{Mn(II)}]_{\mathrm{total}}^{-1}, \quad (1)$$

where the subscript "org" and the lack of any subscript denoted those species in the organic and aqueous phases respectively. The β-diketones were denoted by HA and TOPO by L. The equilibrium constants employed were

$$K_a = [\mathrm{H}^+][\mathrm{A}^-][\mathrm{HA}]^{-1}, \quad (2)$$

$$K_d = [\mathrm{HA}]_{\mathrm{org}}[\mathrm{HA}]^{-1}, \quad (3)$$

$$\beta_n = [\mathrm{MnA}_n{}^{2-n}][\mathrm{Mn}^{2+}]^{-1}[\mathrm{A}^-]^{-n}, \quad (4)$$

$$K_{\mathrm{dm}} = [\mathrm{MnA_2}]_{\mathrm{org}}[\mathrm{MnA_2}]^{-1}, \quad (5)$$

$$K_{\mathrm{ex}} = [\mathrm{MnA_2}]_{\mathrm{org}}[\mathrm{H}^+]^2[\mathrm{Mn}^{2+}]^{-1}[\mathrm{HA}]_{\mathrm{org}}^{-2} \quad (6)$$

$$= (K_aK_d^{-1})^2K_{\mathrm{dm}}\beta_2, \quad (7)$$

$$\beta_{n(\mathrm{org})} = [\mathrm{MnA_2L}_n]_{\mathrm{org}}[\mathrm{MnA_2}]_{\mathrm{org}}^{-1}[\mathrm{L}]_{\mathrm{org}}^{-n}. \quad (8)$$

The distribution ratio in the absence and in the presence of L can generally be written as

$$\begin{aligned} D_0 &= [\mathrm{MnA_2}]_{\mathrm{org}}([\mathrm{Mn}^{2+}]+[\mathrm{MnA}^+]+[\mathrm{MnA_2}])^{-1} \\ &= [\mathrm{MnA_2}]_{\mathrm{org}}[\mathrm{Mn}^{2+}]^{-1}(1+\textstyle\sum\beta_n[\mathrm{A}^-]^n)^{-1}, \quad (9) \\ D &= ([\mathrm{MnA_2}]_{\mathrm{org}}+[\mathrm{MnA_2L}]_{\mathrm{org}}+[\mathrm{MnA_2L_2}]_{\mathrm{org}}) \\ &\quad \times ([\mathrm{Mn}^{2+}]+[\mathrm{MnA}^+]+[\mathrm{MnA_2}])^{-1} \\ &= D_0(1+\textstyle\sum\beta_{n(\mathrm{org})}[\mathrm{L}]_{\mathrm{org}}^n). \quad (10) \end{aligned}$$

The stability constants, β_n, were determined from the data obtained when the $[\mathrm{L}]_{\mathrm{org}}$ was zero or a certain constant value as a function of $[\mathrm{A}^-]$. The adduct formation constants were determined from the data obtained at a certain constant value of $[\mathrm{A}^-]$ as a function of $[\mathrm{L}]_{\mathrm{org}}$. The data were treated by a graphic method previously reported.[1-4] For the determination of the β_1 and β_2 of hexafluoroacetylacetonates, tributyl phosphate was used as the synergist instead of TOPO because TOPO was too effective to achieve suitable conditions.

Results and Discussion

The distribution ratio was measured at various pH values in the absence and in the presence of chromate ions. It was found that the distribution ratio reached a constant value in the absence of chromate if the —log $[\mathrm{H}^+]$ value was lower than 9 and if the agitation interval was shorter than 3 h. This D value was lower than that obtained in the presence of chromate. Thus, the D obtained after an agitation for less than 3 h at —log $[\mathrm{H}^+]$ values lower than 9 was concluded to show the distribution equilibrium of manganese(II) and no extraction of manganese(III).

The extraction curve with benzoylacetone was nearly a straight line with a slope of 2 when the distribution ratio was lower than 10^2; thus, only K_{ex} could be determined form these data. The curve with hexafluoroacetylacetone deviated only slightly from a straight line with a slope of 2 up to its maximum concentration, 0.1 mol dm^{-3}; thus, only K_{ex} and β_1 could be determined.

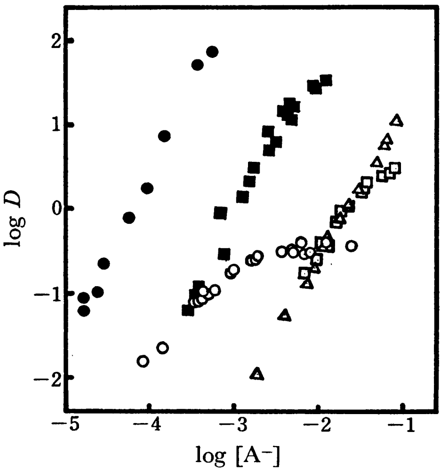

Fig. 1. Representative extraction curves. Org. phase: CCl_4 containing ○ acetylacetone$+5\times10^{-3}$ mol dm^{-3} of TOPO, ● benzoylacetone, □ trifluoroacetylacetone, ■ benzoyltrifluoroacetone, or △ hexafluoroacetylacetone$+1\times10^{-3}$ mol dm^{-3} of tributylphosphate. Aq. phase: 1 mol dm^{-3} $NaClO_4$.

Table 1. Summary of equilibrium constants
Aq. phase: 1 mol dm^{-3} $NaClO_4$. Org. phase: CCl_4. Adduct-forming ligand: trioctylphosphine oxide (TOPO). The data of Mn(II): present work. The other data: Refs. 1—4.

Extractant	Metal ion	log K_{ex}	log β_1	log β_2	log K_{dm}	log $\beta_{1\,(org)}$	log $\beta_{2\,(org)}$
Acetylacetone	Mn(II)	−11.8	4.09	6.98	−1.23	2.96	4.96
log K_a = −8.99	Co (II)	—	—	—	−0.94	1.46	nil
log K_d = 0.40	Ni (II)	—	—	—	−2.0 to −2.5	*ca.* 2	nil
	Cu (II)	−3.73	7.81	14.22	0.83	1.28	nil
	Zn (II)	−11.40	4.58	7.76	−0.38	3.07	4.66
Benzoylacetone	Mn(II)	−8.4	—	—	(>3)[a]	3.81	5.40
log K_a = −8.55	Co (II)	−13.05	4.55	8.14	1.37	3.40	nil
log K_d = 2.73	Ni (II)	−12.84	4.41	9.86	−0.14	3.50	nil
	Zn (II)	−11.36	4.15	7.70	3.50	3.76	nil
Trifluoroacetylacetone	Mn(II)	−10.28	0.94	2.96	−1.44	5.43	9.16
	Co (II)	−8.34	3.50	5.60	−2.14	5.36	7.76
logK_a = −6.90	Ni (II)	*ca.* −9	3.74	6.68	−3.0 to −3.5	*ca.* 5	*ca.* 8
log K_d = −0.19	Cu (II)	−1.26	4.80	9.14	1.40	2.96	nil
	Zn (II)	−8.76	2.72	4.48	−1.44	6.70	nil
Benzoyltrifluoroacetone	Mn(II)	−12.62	0.80	2.63	1.71	6.1	10.4
log K_a = −6.01	Co (II)	−9.66	3.40	5.24	2.06	6.15	9.34
log K_d = 2.47	Ni (II)	−9.52	3.60	6.68	0.76	5.19	8.98
	Zn (II)	−9.02	3.23	5.49	2.45	6.71	nil
Hexafluoroacetylacetone	Mn(II)	−5.0	1.04	—	(>−1)[a]	—[b]	—[b]
log K_a = −4.34	Co (II)	−3.90	1.56	2.32	−1.02	5.19	10.58
log K_d = −1.74	Ni (II)	−4.0	1.78	3.26	−2.1	5.8	10.5
	Cu (II)	−0.61	2.25	3.20	1.39	5.63	9.36
	Zn (II)	−5.2	1.0	—	(>−1)[a]	7.0	11.6

a) Since these values could not be determined, only the lower limit is assumed. b) Too high to be determined by the present experimental procedures; see text.

Figure 1 shows examples of representative extraction curves.

The extraction with these β-diketones was enhanced very much by TOPO. The adduct formation constants of the benzyltrifluoroacetonate were somewhat inaccurate, and those of the hexafluoroacetylacetonate could not be determined within the limits of experimental error. However, since the constants for the adducts with TBP determined instead of those with TOPO (log $\beta_{1(org)}=4.9$ and log $\beta_{2(org)}=9.4$) were rather similar to the corresponding zinc(II) TBP adducts (log $\beta_{1(org)}=5.5$ and log $\beta_{2(org)}=8.5$),[2] the values for the TOPO adducts of the manganese(II) hexafluoroacetylacetonate should be similar to those of the zinc(II) chelates.

The constants obtained are given in Table 1, together with the values previously obtained in our laboratory.[1–4]

From these data, it can be concluded that (i) the Irving-Williams natural order is well established among these β-diketonates, (ii) the K_{dm} values (showing the inverse of the aquophilic tendency when the molar volumes are similar[3]) of the manganese(II) chelates are much higher than those of the nickel(II) chelates and lower than those of the copper(II) chelates; they are approximately in the same order as the values of cobalt(II) and zinc(II) chelates, and (iii) the synergic enhancement with TOPO is similar to that of the zinc(II) chelates or greatest among the metal chelates in Table 1.

As is seen from the present results, these manganese(II) extractions, except for that with benzoylacetone, were poor for various practical purposes when the solvent was carbon tetrachloride. However, since the synergic enhancement was very great, the addition of a synergist such as TOPO and TBP or the use of oxygen-containing solvents such as 4-methyl-2-pentanone (MIBK), the extraction of this metal ion should become effective.

There have been reports on the extraction with these β-diketonates of manganese(II) that the extraction was partial with acetylacetone in benzene,[5] but that it was better when using butanol[6] or by the addition of hydrogen peroxide,[7] and that the extraction with benzoylacetone in benzene was more than 90% at pH values higher than 9.[5] Not much has been reported on the stability constants of manganese(II) β-diketonates which can be compared directly with the present results,[9] except that the log β_1 for the acetylacetonate in a 0.1 mol dm^{-3} medium was 4.01.[9]

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