[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS, THE PENNSYLVANIA STATE COLLEGE]

Studies on Coördination Compounds. V. The Effects of Salt Anion and of Solvent upon the Chelation of β-Diketones[1]

BY LEGRAND G. VAN UITERT, W. CONARD FERNELIUS AND BODIE E. DOUGLAS

RECEIVED JANUARY 2, 1953

The divalent metal salts are extensively associated beyond the degree expected to conform with strong electrolyte behavior in a solution consisting of 75 volume % dioxane and 25 volume % water. This association does not appear to be the case for the nitrate or perchlorate salts of the monochelated divalent cations of Mg, Mn, Co, Zn, Ni, Fe and Cu. The true ratio of the first to the second formation constants, K_{f_1}/K_{f_2}, for the chelate complexes of β-diketones formed in such solutions is obscured by the strong coördination of salt anions and water with the divalent metal salts. As these factors are reduced, the apparent ratio increases. In general the log K_{f_1} and log K_{f_2} values vary linearly with n_2 (the mole fraction of dioxane in solution) and essentially parallel the pK_D values for the enol form of the chelating agent.

Introduction

The effect of the salt anions in solution, and the effect of the solvent itself upon the "measured" formation constants of the chelate compounds formed between a series of divalent metal ions and β-diketones can be demonstrated by varying the salt anions and the mole fraction of water in solution.

The relative coördinating tendencies of the salt anions with the metal ion species that exist in solution can be determined by measuring the formation constants for exchanges of the type

$$MX_2(H_2O)_y + HCh \rightleftarrows HX + MChX(H_2O)_z + (y - z)H_2O$$

in a medium such as 75 volume % dioxane–25 volume % water. In this solution, ion pair formation is extensive even for such highly ionized compounds as tetraisoamylammonium perchlorate.[2] Hence, the differences in the abilities of the metal ions to coördinate anions can be determined from the differences in the formation constants calculated on the assumption of strong electrolyte behavior for the metal salts.[3]

The effect of coördination of the solvent (water principally) to the metal ion can be demonstrated by comparing the values of the first and second formation constants in solutions having different concentrations of water when the perchlorate salts, which most nearly approximate strong electrolyte behavior, are employed.

Experimental

The experimental procedure and calculations are the same as those described previously[4] for the 75 volume % dioxane solutions. Changes in the solvent ratio and the addition of neutral electrolytes are noted in the appropriate parts of the discussion. The data were obtained at 30°.

Discussion

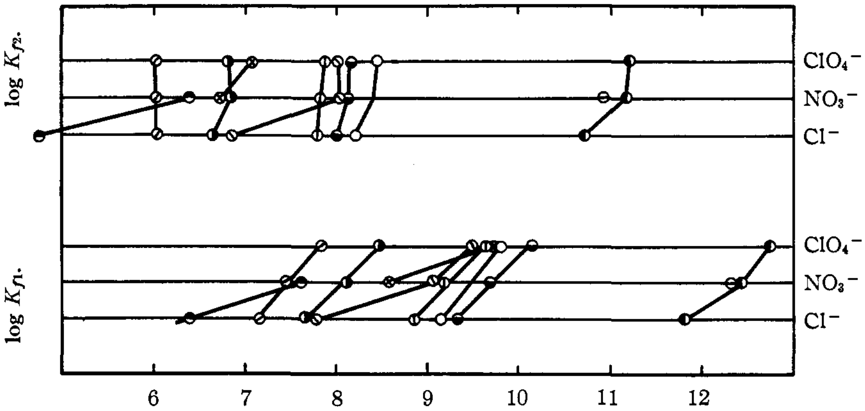

Fig. 1.—The salt anion effect—chloride, nitrate and perchlorate salts *vs.* acetylacetone: ◐, Cu; ⊖, Be; ○, Fe; ◒, Ni; ⦶, Co; ⦸, Zn; ◑, Mn; ⊗, Pb; ◓, Cd; ⊘, Mg.

(a) **The Salt Anion Effect.**—The effect of changing the salt anion in solution in the series Cl^-, NO_3^-, ClO_4^- is illustrated for the case of acetylacetone *vs.* the several metal salts in 75 volume % dioxane solution by Fig. 1. In every case the "measured" first formation constants (log K_{f_1}) increase when the salt anions are varied in the above order. The difference in the values for two salt anions with the same divalent cation is a measure of the relative coördinating ability of the two salt anions with the divalent metal ion. This effect is not as prominent for the monochelated divalent metal ions. With the exception of lead there is little difference in the log K_{f_2} constants for the nitrate and perchlorate salts of the same metal ion. Cadmium, lead, zinc and copper appear to have an exceptional tendency to coördinate salt anions. This tendency is especially evident for the difference between the nitrates and the chlorides. Lead also shows a marked increase in the "measured" formation constant between the perchlorate and the nitrate. It is quite probable that the log K_{f_2} values for the perchlorate salts with the exception of lead are close to the formation constants which would result if the monochelated divalent metal salts act as strong electrolytes. Since there are appreciable differences in the values for the perchlorate salts and nitrate salts for log

---

[1] A portion of a dissertation presented by L. G. Van Uitert in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1952.

[2] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd Ed., Reinhold Publ. Corp., New York, N. Y., 1950.

[3] L. G. Van Uitert and C. G. Haas, Jr., THIS JOURNAL, **75**, 451 (1953).

[4] L. G. Van Uitert, W. C. Fernelius and B. E. Douglas, *ibid.*, **75**, 457 (1953).

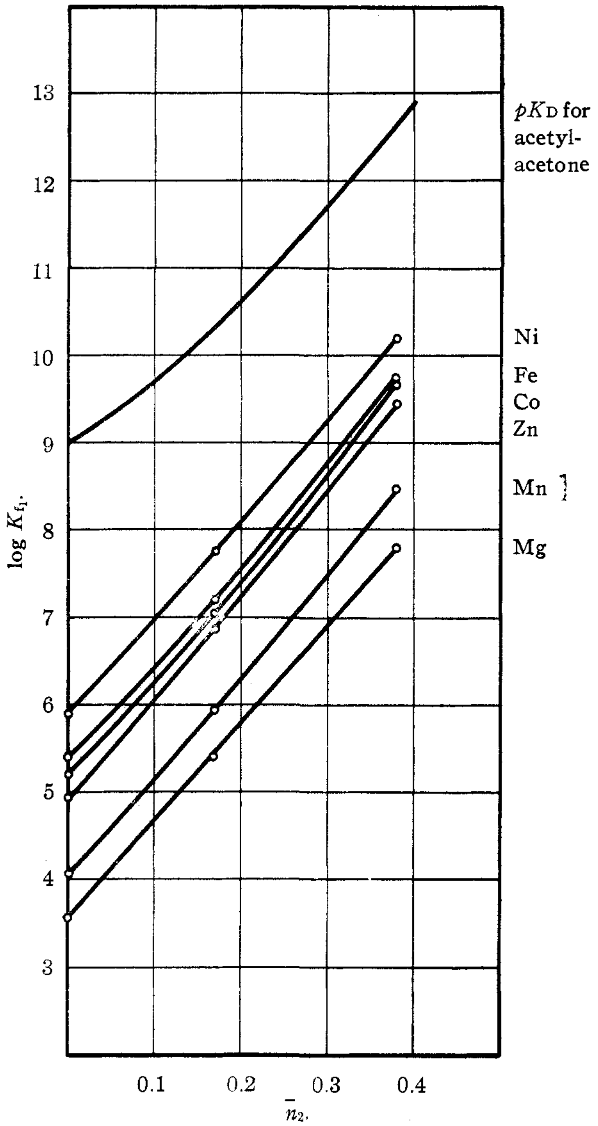

Fig. 2.—log K_{f_1} *vs.* mole fraction dioxane for the acetylacetonate complexes.

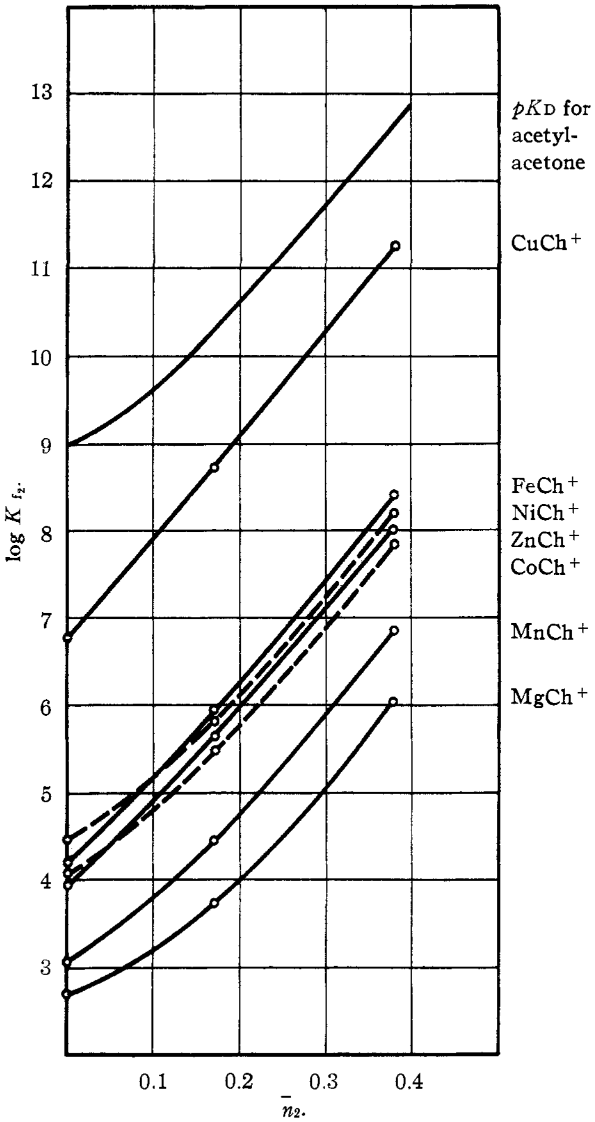

Fig. 3.—log K_{f_2} *vs.* mole fraction of dioxane for the acetylacetonate complexes.

K_{f_1}, the same cannot be said in this case. The tendency of the perchlorate ion to coördinate with the unchelated divalent metal ion is larger than would be expected from the defined "strong electrolyte" behavior previously discussed.[3] This tendency is demonstrated by adding 2×10^{-3} mole of $NaClO_4$ to the standard chelation titration solutions for $Ni(ClO_4)_2$ and $Zn(ClO_4)_2$ *vs.* acetylacetone. In each case the "measured" log K_{f_1} value was $\sim$0.3 log unit lower as a result. Thus doubling the stoichiometric concentration of perchlorate ion in the solution doubled the degree of coördination of the zinc ion. In the case of $Zn(ClO_4)_2$ additional titrations were performed: 2×10^{-3} mole of NaCl, NaBr, NaI and $NaNO_3$ in turn were added in place of the $NaClO_4$. The *p*H meter readings were compared where $\bar{n} = 0.5$[3] for the titrations employing these anions. The differences indicated that the ratios in which the different salt anions coördinate are approximately: $ClO_4^-:NO_3^-:I^-:Br^-:Cl^- = 1:1.5:2:7:15$. The order is such as to indicate that the zinc salts are increasingly dissociated in 75 volume % dioxane solution in the order of increasing anion size for the monovalent anions.

(b) **The Solvent Effect.**—The effect of changing the water–dioxane ratio in solution has been measured using the perchlorate salts to ensure the minimum deviation from strong electrolyte behavior. In each case acetylacetone was used as the chelating agent. The titrations were carried out for Mg, Mn, Co, Zn, Ni, Fe and Cu in the solvent mixtures containing 100% water, 50 volume % dioxane (n_2 = 0.172), and 75 volume % dioxane (n_2 = 0.380). The coördination of salt anions to these divalent cations would be expected to decrease as the solvent becomes more polar. Hence, since the divalent ion is more strongly coördinated than the monovalent ion as shown above, one would expect an increase in the values of log K_{f_1} − log K_{f_2}. However, the difference between them increases as the mole fraction of dioxane is *increased*. This behavior is probably due to a reduction in the effective hydration of the divalent cation. The

TABLE I

	n_2 = 0.380 dibenzoylmethane		n_2 = 0.380 acetylacetone		n_2 = 0.170 acetylacetone		n_2 = 0.00 acetylacetone	
	log K_{f_1}	log K_{f_2}	log K_{f_1}	log K_{f_2}	log K_{f_1}	log K_{f_2}	log K_{f_1}	log K_{f_2}
$Mg(ClO_4)_2$	8.97	7.61	7.81	6.09	5.40	3.74	3.47	2.38
$Mg(NO_3)_2$	8.54	7.67	7.49	6.09				
$MgCl_2$			7.17	6.08				
$Cd(NO_3)_2$	8.67	7.96	7.64	6.42				
$CdCl_2$			6.42	4.78				
$Mn(ClO)_2$	9.69	8.47	8.50	6.84	5.96	4.44	4.05	3.02
$Mn(NO_3)_2$	9.32	8.47	8.15	6.87				
$MnClO_2$	8.95	8.35	7.71	6.68				
$Zn(ClO_4)_2$	10.59	9.41	9.52	8.05	6.86	5.63	4.92	3.95
$Zn(NO_3)_2$	10.23	9.42	9.11	8.09				
$ZnCl_2$	8.99	8.24	7.79	6.89				
$Co(ClO_4)_2$	10.74	9.79	9.68	7.92	7.07	5.48	5.23	4.05
$Co(NO_3)_2$	10.35	9.70	9.22	7.86				
$CoCl_2$	9.97	9.63	8.88	7.83				
$Ni(ClO_4)_2$	11.14	9.91	10.19	8.21	7.71	5.87	5.91	4.49
$Ni(NO_3)_2$	10.83	9.89	9.70	8.15				
$NiCl_2$	10.46	9.71	9.34	8.03				
$Fe(ClO_4)_2$	11.15	10.35	9.71	8.48	7.20	5.94	5.38	4.20
$FeCl_2$	10.64	...	9.19	8.25				
$Cu(ClO_4)_2$	...	...	(12.78)	11.24	10.48	8.72	7.99	6.73
$Cu(NO_3)_2$	...	...	12.46	11.20				
$CuCl_2$	12.98	12.00	11.85	10.74				
$Pb(ClO_4)_2$	10.73	9.46	9.73	7.10				
$Pb(NO_3)_2$	9.75	9.04	8.60	6.77				
$Be(NO_3)_2$	13.62	12.41	12.36	10.94			7.95	6.57

difference can be expected to increase markedly as the concentration of water in solution approaches zero.

The log K_{f_1} and log K_{f_2} values for the several chelate compounds have been plotted along with the apparent pK_D[5] values for the chelating agent (acetylacetone) as a function of the mole fraction of dioxane in Figs. 2 and 3. The log K_{f_1} values for a given cation essentially fall on a common line. The log K_{f_1} values for Cu are not plotted since the recorded values are the estimated "minimum" values in this case.

The log K_{f_2} values fall on lines showing a pattern similar to those for log K_{f_1} for the cases of the monochelated divalent metal ions Cu, Fe and Zn when they are plotted against n_2, the mole fraction of dioxane in solution. In the cases of Ni, Co, Mn and Mg the values measured in water are larger than would be expected. These ions are the four monochelated divalent metal ions that show the least tendency to coördinate with salt anions (Fig. 1).

(c) **Temperature Coefficients.**—Measurements were also made at 50° to determine the value of pK_D for acetylacetone and the formation constants for this chelating agent with $Zn(ClO_4)_2$, $Ni(ClO_4)_2$, $Cu(ClO_4)_2$ and $Be(NO_3)_2$ in aqueous solution. The differences between the calculated constants at 30 and 50° were of the same magnitude as the possible experimental error. In all cases the calculated temperature coefficient was less than 0.1 log unit and cannot be used for the calculation of thermodynamic data due to the large uncertainty that exists in the values.

Acknowledgment.—The authors gratefully acknowledge financial support furnished for this work by the United States Atomic Energy Commission through Contract AT(30-1)-907.

STATE COLLEGE, PA.

---

[5] L. G. Van Uitert with Charles G. Haas, W. Conard Fernelius and Bodie E. Douglas, THIS JOURNAL, **75**, 455 (1953).