[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF KING COLLEGE]

Equilibrium Between the Complexes of Tervalent Manganese with 2,4-Pentanedione

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A spectrophotometric study has been made of the changes occurring when trispentanedione manganese(III) in aqueous pentanedione is subjected to varying acidity. It has been shown that the tris complex changes reversibly to a bispentanedione diaquo complex, and the equilibrium constant for the process has been determined. An approximate value for the acidic ionization constant of the diaquo complex also has been established. The formal acid ionization constant of the diketone has been measured and found to be consistent with the natural *p*H values of solutions of the complex in aqueous pentanedione. The bispentanedione diaquo complex has been isolated; it is believed to be the first example of a cationic complex of tervalent manganese.

Like many other tervalent ions, manganese(III) ion forms a neutral complex with 2,4-pentanedione which is only moderately soluble in water but quite soluble in ether, alcohol, acetone and other organic solvents.[1] Contrary to published statements that the compound is moderately stable toward acids, it was observed that a solution of the compound in aqueous pentanedione undergoes a progressive change in color when the solution is acidified. A saturated solution in aqueous pentanedione is coffee-brown; upon gradual addition of sulfuric acid, the color lightens, passes through a golden hue, and at a *p*H of about 3 becomes greenish-yellow. The changes are reversible.

This behavior strongly recalls the corresponding changes in the trioxalato- and trimalonato-manganese(III) salts which have been studied by the author and his students.[2,3] In both of these cases the reaction involves the replacement of one of the bivalent complexing anions by two molecules of water

$$Mn(C_2O_4)_3^{3-} + 2H_2O \rightleftharpoons Mn(C_2O_4)_2(H_2O)_2^- + C_2O_4^{2-}$$

Equilibrium constants were determined spectrophotometrically at 0°, the values being 0.0038 and 0.057, respectively, for the oxalate and malonate systems.

A further indication that a similar replacement might be occurring in the pentanedione complex was furnished by a preliminary study of the manganese(II–III) electrode potential in the presence of pentanedione at various acidities. These measurements showed close to a second-power hydrogen-ion dependence of the electrode potential at *p*H values below 7, which is most simply interpreted by the electrode reaction

$$Mn^{2+} + 2HPn + 2H_2O \rightleftharpoons MnPn_2(H_2O)_2^+ + 2H^+ + e$$

(In the sequel, Pn^- will be used to represent the univalent anion of 2,4-pentanedione. For brevity, the neutral complex containing three such anions will be referred to as the tris-complex. The cation having two pentanedione anions will be called the bis-complex.)

A spectrophotometric study of the system was therefore undertaken. Because of instability of the complex in water alone, it was necessary to use aqueous pentanedione solutions at least 0.05 F as solvent. Weighed samples of the pure tris-complex were dissolved and adjusted to various *p*H values by addition of small amounts of dilute sulfuric acid or sodium hydroxide. The absorption was then measured on a Beckman model DU spectrophotometer, having the solvent in the comparison cell.

The choice of a suitable wave length was made from a study of the absorption spectrum of the complex solutions at various acidities over the range of wave lengths from 1200 to 325 mμ. It was apparent that, at 1100 mμ, the tris-complex has a flat maximum with a molecular extinction coefficient of 96 to 100, depending upon the solvent used, and that this drops almost to zero when *p*H is reduced to about 2. In work to be subsequently reported in detail, the bis-complex has been isolated as the pure hydrated perchlorate, and the selection of this wave length fully justified.

Theory.—For the reasons given, the reaction was assumed to be

$$MnPn_3 + 2H_2O + H^+ \rightleftharpoons MnPn_2(H_2O)_2^+ + HPn$$

the two water molecules being included to preserve a coördination number of 6, and also in analogy with the other known diaquo complexes of manganese. The equilibrium equation is then

$$\frac{[MnPn_2(H_2O)_2^+][HPn]}{[MnPn_3][H^+]} = K \qquad (1)$$

The hydrogen-ion concentrations were measured with a Beckman *p*H meter, Industrial Model, and the free pentanedione concentration was known from the method of preparation of the solvent, with correction for the additional amount formed in the displacement reaction. No attempt was made to differentiate the keto–enol concentrations.

We let e_3 be the molecular extinction coefficient of the pure tris-compound, e_2 that of the bis-ion, and e the formal value based on the measured optical density and known formality in manganese. These e's are defined by the relation $\log_{10} I_0/I = ecl$, where c is in moles per liter and l in cm. We let the concentrations of the bis-ion and the tris-compound be represented by c_2 and c_3, respectively. In the equilibrium mixture $\log_{10} I_0/I = (e_2c_2 + e_3c_3)l = e(c_2 + c_3)l$. We then find, for equilibrium

$$\frac{e_3 - e}{e - e_2} \times \frac{[HPn]}{[H^+]} = K \qquad (2)$$

After the e_3 and e_2 values were established, as will be subsequently shown, it was found that this equation gave consistent values for K for *p*H values as high as about 5.5. Above this point there was a steady increase in the apparent K values, the exact

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[1] G. Urbain and A. Debierne, *Compt. rend.*, **129**, 3046 (1899); F. Gach, *Monatsh.*, **21**, 110 (1900).

[2] G. H. Cartledge and W. P. Ericks, THIS JOURNAL, **58**, 2065 (1936).

[3] G. H. Cartledge and P. M. Nichols, *ibid.*, **62**, 3057 (1940).

*p*H at which the deviation began depending upon the concentration of free pentanedione.

As a hypothesis, it was assumed that at higher *p*H values the bispentanedione diaquo ion functions as a weak acid in accordance with the equation

$$\mathrm{MnPn_2(H_2O)_2^+ \rightleftharpoons MnPn_2(H_2O)(OH) + H^+}$$

This would be in accordance with similar behavior of other aquo complexes,[4,5] and would account for the obvious excessive replacement reaction at higher *p*H's.

For this acidic ionization we have

$$\frac{[\mathrm{MnPn_2(H_2O)(OH)}][\mathrm{H^+}]}{[\mathrm{MnPn_2(H_2O)_2^+}]} = K' \qquad (3)$$

whence

$$\frac{[\mathrm{MnPn_2(H_2O)_2^+}]}{[\mathrm{MnPn_2(H_2O)_2^+}] + [\mathrm{MnPn_2(H_2O)(OH)}]} = \frac{[\mathrm{H^+}]}{K' + [\mathrm{H^+}]} \qquad (4)$$

There is no way to isolate the hydroxo-complex for an exact determination of its extinction coefficient, since the solutions form turbidities or precipitates at *p*H values that are high enough to produce it in adequate concentrations. At the higher *p*H's involved, both of the bis-complexes (diaquo and hydroxo-aquo) are present in only small proportions, relative to the tris-complex. The assumption is therefore made that, since the bis-diaquo complex has an almost negligible extinction coefficient at the wave length employed (1100 mμ), the total bis-complex concentration from equation (4) may be substituted in equation (1) and the value of e_2 then applied to the total bis-complex concentration without sensible error.

This substitution gives, after rearrangement

$$\frac{e_3 - e}{e - e_2} \times \frac{[\mathrm{HPn}]}{K} - [\mathrm{H^+}] = K' \qquad (5)$$

Since K' appears as a difference of two terms that, in many cases, are of similar magnitude, it cannot be evaluated with a high degree of accuracy. It is only a correction term for the higher *p*H range, however, and the average of the values found at higher *p*H's serves quite well to rectify the data. The value of K' so found is 5×10^{-8}, the accurate value of K for higher acidities being used in the calculation.

Since pentanedione itself ionizes appreciably in the range of higher *p*H values, a potentiometric titration of a solution of purified pentanedione was made, from which the thermodynamic ionization constant of 1.16×10^{-9} was determined at a salt formality of about 0.2. This value of K_a was used in calculating the concentration of the free pentanedione from its known formality and the measured *p*H.

In order to show concisely the agreement of the numerous measurements with the theory developed the theoretical values of the formal extinction coefficient for 1100 mμ of equilibrium mixtures were then calculated from equation (5) and plotted as continuous curves in Fig. 1.

Results.—As solvents, aqueous solutions of 1.0, 0.5, 0.25, 0.10 and 0.05 formal pentanedione were used. At the lower *p*H values, the absorption was too low to be measured precisely in the 1-cm. cells; and at both low (2.5) and relatively high *p*H's the solutions faded slowly, making accurate measurements difficult, particularly above *p*H 7. For the determination of K at *p*H's below 5.5, 34 measurements were made with the following results, for room temperatures near 25°:

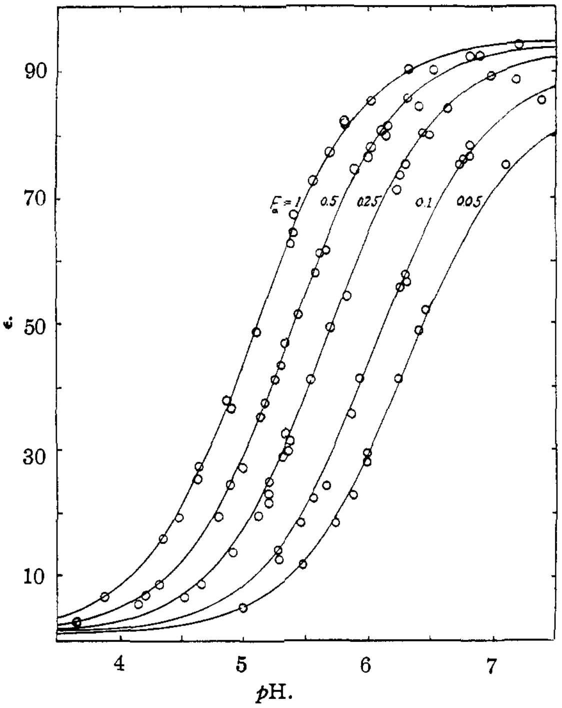

Fig. 1.—Observed and calculated values of the formal extinction coefficient, *e*, of equilibrium mixtures at various acidities in pentanedione of various concentrations. Circles are the measured values; the curves are calculated from equation 5.

Formality of HPn (F_a)	$10^{-5}\,K$	Number of points
1.000	1.20 ± 0.05	12
0.500	1.22 ± .04	11
.250	1.25 ± .07	7
.100	1.24 ± .02	4

Average $K = 1.22 \times 10^5$ (± 0.05)

The values of K' for the acidic ionization of the diaquo ion were derived from 11 points measured on solutions of 0.005 *F* complex in 0.050, 0.100 and 0.250 *F* pentanedione at *p*H's of 6.26 to 8.00. The average value was 5×10^{-8} (± 1).

Figure 1 shows the results of a considerable number of measurements that were obtained after the peculiarities of the system had been determined. The continuous curves give the theoretical values of the formal extinction coefficient calculated from equation (5) for the following conditions: (a) solvent pentanedione has the formality indicated before addition of solute; (b) formality in manganese(III) is 0.005 *F;* (c) pentanedione concentration is corrected for fractional ionization above *p*H 7; (d) activity coefficients are disregarded, since in none of the solutions is the ionic strength sufficiently high to be significant. The probable error in *p*H measurements was 0.03 unit, in spite

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[4] J. N. Brönsted and C. V. King, *Z. physik. Chem.*, **130**, 699 (1927).

[5] J. N. Brönsted and C. V. King, *ibid.*, **134**, 97 (1928).

of frequent calibration. This error is approximately indicated by the radius of the circles. Extinction measurements were also somewhat difficult to make at 1100 mμ, owing to the sensitivity of the instrument to air currents. In spite of these difficulties and the inherent instability of certain of the mixtures, only an occasional point falls outside the presumed reliability of the data, leaving no doubt, therefore, of the correct formulation of the reaction.

A further application of the equilibrium relationships gives a value for the natural *p*H of solutions of the tris-complex in aqueous pentanedione solutions of varying formality. The partial replacement of the third pentanedione ion by water molecules represses the ionization of the solvent to an extent that may be calculated and compared with the measured *p*H values, as follows.

The replacement reaction may be expressed by the equation $MnPn_3 + 2H_2O \rightleftarrows MnPn_2(H_2O)_2^+ + Pn^-$, the corresponding mass-action expression being

$$\frac{[MnPn_2(H_2O)_2{}^+][Pn^-]}{[MnPn_3]} = K'' = KK_a \qquad (6)$$

The constant K'' may readily be seen to be equal to the constant K of equation (1) multiplied by the K_a for the acidic ionization of pentanedione, $[H^+][Pn^-]/[HPn] = K_a$. By suitable manipulation of these equations and the additional conditions equations that are applicable, one may obtain the equation

$$K = K_aF_a{}^2/[H^+]\ (F_c[H^+] - K_aF_a) \qquad (7)$$

in which F_a is the formality of pentanedione and F_c the formality in manganese(III). It is unnecessary to consider equation (3) in the derivation, since its effect is entirely negligible for the conditions considered.

The natural *p*H of many of the equilibrium solutions used was measured, with the results shown in Table I. The calculated values were obtained by used of equation (7).

TABLE I

NATURAL *p*H OF EQUILIBRIUM MIXTURES

F_a	F_c	*p*H, calcd.	*p*H, obsd.
1.0	0.005	5.82	5.80, 5.80
0.5	.005	6.12	6.18, 6.15, 6.17, 6.12, 6.12
.5	.0025	5.96	6.00
.5	.001	5.73	5.75
.25	.005	6.44	6.45, 6.44, 6.50
.1	.005	6.82	6.83, 6.81, 6.78, 6.72, 6.74, 6.83
.05	.005	7.12	7.10, 7.09

It is to be noted that the value of K calculated from the absorption measurements does not involve the K_a value, which was independently determined. Since the calculated *p*H values in Table I are based on this K_a value as well as on the optical K value, the observed concordance of the *p*H's is good substantiation of both constants.

Discussion.—The identification of the bis-complex as required by the equilibrium conditions is believed to furnish the first example of a stable cationic complex of tervalent manganese. The valence and coördination-number relationships make its structure similar to those of the cationic pentanedione complexes with boron, silicon and titanium.[6]

The magnitude of the acid ionization constant of the bispentanedione diaquo ion is of interest in comparison with the values reported for other aquo ions.[4,5,7] For aquo complexes of the tervalent ions of the transition elements, *pK* values in the range of 2 to 6 have been found for the first ionization, the acid strength depending upon the valence and constitution of the acid ion. The rather high *pK* value here found for the bispentanedione diaquo manganese(III) ion (*pK* 7.3) is consistent with the univalence of the ion and the close proximity of the ionizable hydrogen ions to the coördinated oxygen atoms of the pentanedione.

To compare the free energy of the displacement reaction with the results previously given[2,3] for the oxalato and malonato systems it is necessary to use the mass-action equation in the form of equation (6). From the results obtained

$$\frac{[MnPn_2(H_2O)_2{}^+][Pn^-]}{[MnPn_3]} = KK_a = 1.42 \times 10^{-4} \qquad (8)$$

from which $\Delta F°_{298.1} = 5250$ cal.

The corresponding values are 3020 cal. for the oxalate reaction at 0° and 1550 cal. at 0° for the malonate. Though the temperatures are different, this may indicate that the third pentanedione ion is bound appreciably more firmly than the third oxalate ion. Preliminary potentials for the manganese(II–III) electrode indicate also that the binding of the first two anions is considerably firmer in the pentanedione system.

Experimental

Materials.—The pentanedione used was generously donated by the Carbide and Carbon Chemicals Division of the Union Carbide and Carbon Corporation. To remove small amounts of acetic acid, the liquid was agitated with successive small portions of 2 *N* sodium hydroxide until the aqueous phase remained faintly alkaline. After being washed with water, the sample was dried over anhydrous sodium sulfate and distilled through a modified Vigreux column. The distillate was water white and the boiling range was 136.5–137° (723 mm.). Fresh portions were prepared frequently.

Trispentanedione manganese(III) was prepared by reaction of theoretical proportions of potassium permanganate and manganous sulfate in the presence of a slight excess of pentanedione and at a regulated *p*H of about 5.0.[8] This method of preparation is far better than the earlier procedure depending upon the reaction of higher oxides of manganese with pentanedione. The well crystallized product was washed first with 0.1 *F* aqueous pentanedione, then with small portions of acetone and ether to hasten the drying process. This raw product analyzed about 99 per cent. pure, but was recrystallized from hot acetone for use in the measurement of the absorption spectrum. For analysis, a sample was fumed with nitric acid and sulfuric acid, diluted to volume, and aliquots were converted to permanganate by potassium periodate for spectrophotometric determination. Analysis of the recrystallized compound gave: Mn 15.59%; theoretical 15.59%.

Dissociation Constant of Pentanedione.—The potentiometric titration of aqueous pentanedione made it apparent that neither of the dissociation constants given in the "International Critical Tables" is correct, these having been

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[6] W. Dilthey, *Ann.*, **344**, 300 (1905); *J. prakt. Chem.*, [2] **111**, 147 (1925).

[7] Compare the discussion by J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941, pp. 66 ff.

[8] G. H. Cartledge, U. S. Patent No. 2,556,316.

based upon conductivity measurements on material that must have contained some acetic acid. Accordingly, a 0.5 *F* solution was prepared from freshly purified pentanedione and titrated with approximately 1.0 *N* sodium hydroxide, using the Beckman blue-glass electrode. The end-point break was between *p*H's of 10 and 12, with the inflection at 11.2, the meter having been approximately calibrated for high *p*H values. Owing to unavoidable absorption of carbon dioxide during the titration, this operation was conducted rapidly. A second portion of pentanedione was then taken and half the indicated quantity of sodium hydroxide was added. The *p*H of this mixture was carefully measured. The titration curve is very flat in this region, and a slight carbon dioxide error in the first titration could affect the *p*H value at the midpoint by only a small amount, probably less than 0.1 *p*H unit. The *p*H observed was 8.81, the salt being 0.2 *N*. The assumption of an activity coefficient of 0.75 for the pentanedione anion at this concentration gives 1.16×10^{-9} as the *formal* dissociation constant, that is, without consideration of the fraction enolized. This corresponds to a pK_a of 8.93. This value is in excellent agreement with the value 1.17×10^{-9} (± 0.02) reported by Eidinoff.[9]

The Molecular Extinction Coefficient of the Tris Complex.—The absorption spectrum of recrystallized complex was measured in 0.1 *F* pentanedione in 95% ethanol. The results are shown in Fig. 2. In addition, the absorption at 1100 mμ was measured in ethyl ether, cyclohexane and various concentrations of pentanedione in alcohol to determine whether the absorption varied largely with the nature of the solvent. Only slight differences were observed at the chosen wave length of 1100 mμ. Several determinations of the extinction coefficient were therefore made in alcoholic pentanedione, using recrystallized complex. With pentanedione concentrations of 0.1 and 0.2 *F*, and complex concentrations of 0.01 and 0.005 *F*, the values 96.0 and 96.4 were obtained. The mean value 96.2 was used for e_3 in the computations.

The e_2 value for the bispentanedione diaquo complex was evaluated by bringing the aqueous equilibrium mixtures down to a *p*H 2 with sulfuric acid. In attainable concentrations of complex this gave too low an absorption to be measured precisely, but the value is so small that even a considerable relative error has no significance for the equilibrium calculations. As a result of many measurements at 1100 mμ, the value $e_2 = 1.0$ was taken for the calculations.

Experiments were made to determine whether the solvent in the comparison cell should be adjusted to correspond to the *p*H of the solution being measured. No measurable absorption was found at 1100 mμ when the pentanedione solutions were varied in the *p*H range of 2 to 8.

Measurements on Equilibrium Mixtures.—The solutions were prepared, for the most part, by placing a weighed sample of the tris-compound in a volumetric flask, adding sufficient purified pentanedione to give the desired formality, shaking until the solid dissolved and then diluting to the mark with distilled water. In earlier experiments the pentanedione solution was first prepared and then added to the solute. The solid is difficultly wetted by the more dilute solutions, however, so that a small portion failed to dissolve rapidly. This necessitated the filtration and analysis of the solution for precise calculations from the absorption data. For producing the desired *p*H's, portions of the solution were adjusted by addition of very small volumes of 1 *N* sulfuric acid or freshly prepared sodium hydroxide. Judging from the color changes and the response of the *p*H meter, equilibrium was established instantaneously and reversibly. When adding base, the mixture was vigorously agitated to avoid disturbances due to excessive local alkalinity. Solutions were adequately stable over most of the *p*H range required, but reproducibility closer than about 2% was difficult to obtain by alkalizing the solutions above *p*H 7. To eliminate possible formation of films due to decomposition, the cells were cleaned with acid and hydrogen peroxide after each use.

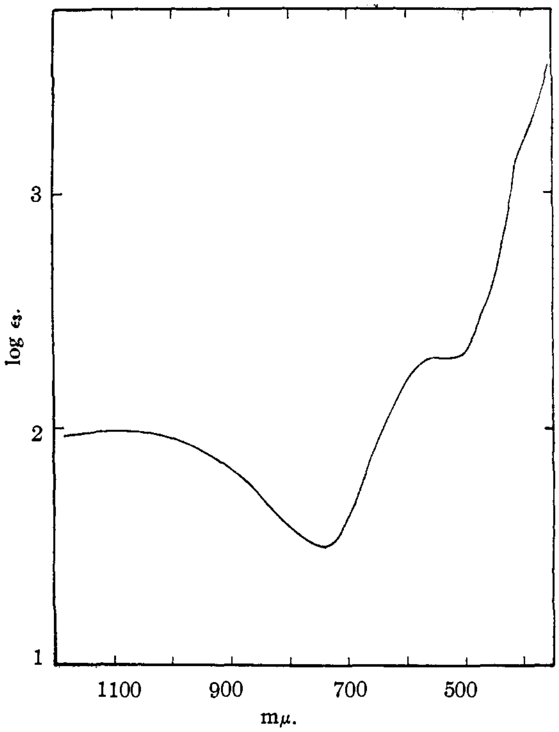

Fig. 2.—Absorption spectrum of trispentanedione manganese(III) in 0.1 *F* pentanedione (alcoholic).

Isolation of the bispentanedione complex was accomplished by trituration of the tris-compound with 1 *M* perchloric acid in slight excess of the theoretical quantity, continuing the addition until *p*H equalled 2.5 and ceased to rise after continuing the grinding for about a minute. The suspension was then extracted once with ether in a separatory funnel to remove most of the pentanedione liberated, filtered, washed with a minimum quantity of acetone and then with ether saturated with water. Details of the preparation, analysis and properties of the new compound will be separately reported. Analysis showed the product to be essentially pure $\{MnPn_2(H_2O)_2\}ClO_4 \cdot 3H_2O$. The salt is olive-green in color and very soluble in many solvents, but only minutely soluble in ether.

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[9] M. L. Eidinoff, THIS JOURNAL, **67**, 2072 (1945).