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The Malonatomanganiates

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In this Laboratory we are making a systematic study of the ability of manganese to form complex ions, particularly when it is in the trivalent and quadrivalent states.[1] The work on oxalato complexes in the preceding papers made it clear that the stability of the manganiates is of an entirely different order from that of the chromic and cobaltic complexes of analogous composition. This difference is found both in the stability with respect to thermal or photochemical decomposition, and also in the extent of dissociation of the complexes into their constituent ions. In the present paper the work is extended to malonato complexes of trivalent manganese. We have prepared pure specimens of both the anhydrous and hydrated forms of potassium dimalonatodiaquomanganiate, determined some of their properties, and measured spectrophotometrically the equilibrium between the di- and trimalonatomanganiates according to the reaction

$$[Mn(C_3H_2O_4)_3]^{---} + 2H_2O \rightleftharpoons [Mn(C_3H_2O_4)_2(H_2O)_2]^{-} + C_3H_2O_4^{--}$$

Preliminary determinations of the electrode potentials in the oxalato and malonato systems have also been made.

Potassium Dimalonatodiaquomanganiate.—Complexes of this type were prepared by Meyer and Schramm,[2] though their procedure did not give pure products and they were unable to obtain the potassium salt sufficiently pure for analysis. In the first paper cited in ref. 1, Cartledge and Ericks described a procedure which gave a pure product of the formula $K[Mn(C_3H_2O_4)_2(H_2O)_2]\cdot 2H_2O$. We have found it possible to prepare the salt in good yield (70%) in a much shorter time by the following modification of the details of preparation.

To 200 ml. of water in a 500-ml. Erlenmeyer flask at room temperature is added 12 g. of malonic acid. Then 6.32 g. of 60-mesh potassium permanganate is added gradually, shaking the mixture continuously. When about four-fifths of the permanganate has been added, the reaction is allowed to proceed until the solution is reddish-brown, the temperature being reduced slowly to about 5° to moderate the reaction. At this point the rest of the permanganate is added and the reaction is allowed to complete itself at 0°. Just as the last of the permanganate color is fading to a greenish-brown, the solution is filtered on a previously cooled Büchner funnel. The filtrate is again placed in the freezing mixture until it begins to freeze, when 50 ml. of ice-cold 95% alcohol is added. Crystallization begins almost at once. After it is well started, 50 ml. more alcohol is added. The solution is left in a freezing mixture (−10°) and stirred by a motor-driven stirrer for about an hour. The crystals are then rapidly filtered and thoroughly washed with 50% alcohol, 95% alcohol, and ether. It is well to leave the crystals in a vacuum desiccator in the dark for at least an hour, as all manganese complexes decompose rapidly if not scrupulously freed from moisture and the organic solvents. The yield is about 10 g.

Preparation of the Anhydrous Salt, $K[Mn(C_3H_2O_4)_2(H_2O)_2]$.—This compound was prepared for the first time by the reaction of stoichiometric quantities of potassium permanganate and malonic acid in absolute methyl alcohol. One-hundredth of a mole (1.58 g.) of potassium permanganate and 0.025 mole (2.60 g.) of malonic acid were shaken with about 150 ml. of absolute methyl alcohol. A crop of olive-green crystals formed in a few minutes, but it was necessary to allow the mixture to stand for about three days at 5° to complete the reaction. The crystals were washed with absolute methyl alcohol.

The product consisted of very fine olive-green crystals and appeared homogeneous under the microscope. The yield was about 90%. When the salt was added to methyl alcohol containing about one-third water, it recrystallized in the usual needles characteristic of the hydrated form.

Anal. Analyses were made by the procedures previously described,[1] except for the determination of the malonate ion. Willard and Young[3] have shown that the direct titration of malonic acid by potassium permanganate is unsatisfactory. Formic acid is produced along with carbon dioxide and an indefinite end-point is obtained. The titration has been studied also by Hatcher and West[4] and by Cameron and McEwan.[5] We have found that a satisfactory determination may be made by direct titration with permanganate in a hot, strongly acid solution.

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[1] Cartledge and Ericks, THIS JOURNAL, **58**, 2061, 2065, 2069 (1936).

[2] Meyer and Schramm, *Z. anorg. Chem.*, **123**, 56 (1922).

[3] Willard and Young, THIS JOURNAL, **52**, 132 (1930).

[4] Hatcher and West, *Trans. Roy. Soc.*, **21**, 269 (1927).

[5] Cameron and McEwan, *Proc. Chem. Soc.*, **26**, 144 (1910).

The sample is added to 100 ml. of water, followed by 20 ml. of concentrated sulfuric acid. A few ml. of standard potassium permanganate is added and the solution is heated to 80–90°; reaction proceeds rapidly as the remaining solution is added. In the first titration only an approximate end-point is located. The titration is then repeated, nearly all of the required permanganate being added at once. Near the end, the solution is added only a few drops at a time, and the end-point is taken when the color persists for a minute while the solution is boiled. Titration of malonic acid by this procedure showed that the equivalent weight of the malonate ion is 17 g. in the reaction, which agrees with the oxidation to carbon dioxide and formic acid

$$C_3H_4O_4 + 3(O) \longrightarrow 2CO_2 + HCOOH + H_2O$$

Typical analyses of the hydrated and anhydrous complexes were as follows:

	Hydrated		Anhydrous	
	Found	Calcd.	Found	Calcd.
K^+	10.56	10.57	11.76	11.71
Mn^{+++} (vol.)	14.73	14.83	16.70	16.44
$C_3H_2O_4^{--}$	54.74	55.13	...	...

As obtained by very slow crystallization, the hydrated salt forms almost black crystals, whereas the form ordinarily produced by the procedure described is a crystalline powder of dark bronzy-green color. Isomeric forms of different color or crystal habit have not been observed, in contrast to the behavior of the corresponding oxalato salt. The complex dissolves readily in ice water, but almost instantaneously decomposes and precipitates as a hydroxy compound of variable composition. In 0.05 *M* malonic acid, however, the salt dissolves without decomposition, the solution being golden yellow if dilute. The presence of malonate ions is necessary for the preservation of the complex, for when it is dissolved in 0.01 *N* nitric acid precipitation occurs, although the dioxalato salt can be dissolved in nitric acid without difficulty. This difference evidently arises in a greater dissociation of the malonato complex into its constituent ions. Dilute solutions in malonic acid have almost the same absorption spectrum in the visible region as the corresponding oxalato salt, with a maximum absorption at 460 mμ (molecular extinction coefficient, 125). The solution is rather rapidly decomposed in ultraviolet light.

The high reactivity of the complex is indicated by the following transformations, which take place almost instantaneously: sirupy phosphoric acid gives the violet phosphoric acid complex; potassium cyanide in excess gives the hexacyano complex; hydrofluoric acid in excess gives the pink pentafluo-aquo complex; catechol, cupferron, and salicylic acid also give complexes. The exact composition of these substances is now being investigated.

Solubility in Malonic Acid.—Five hundredths molar malonic acid was agitated with a considerable excess of the hydrated salt at 0° for ten minutes, when a portion of the solution was withdrawn, filtered, and analyzed. This was repeated until successive analyses showed that the solution was saturated. Analyses were made spectrophotometrically on a ten-fold dilution of the saturated solution. The saturated solution was found to contain 0.072 mole per liter.

The Trimalonatomanganiate.—Meyer and Schramm[2] reported the formation of a trimalonatomanganiate by mixing stoichiometric proportions of dimalonato salt and potassium malonate, with just enough water to moisten the mixture. Red crystals were obtained, but they were always impure. We have made a variety of attempts to obtain a pure product, but without success. In one procedure stoichiometric proportions of potassium permanganate, malonic acid, and potassium malonate were allowed to react, but the only crystals isolated were the green dimalonato salt, although the solution was deep red. The same result was obtained when the dimalonato salt was dissolved in various buffers containing an excess of potassium malonate. Neither by precipitation with alcohol nor by slow evaporation could the red salt be isolated. A few red crystals of a double complex were obtained from the buffered solutions by the addition of hexamminecobalti chloride and alcohol, but the main product was green. We have also tested the method used by Meyer and Schramm. By sucking off the water after a short time and washing the residue in the usual way, a reddish powder was obtained which was contaminated by unchanged green salt. Neither by washing with alcohol–water mixtures nor by recrystallization could the green compound be eliminated.

Fortunately, it is not necessary to isolate the red salt for the measurement of the equilibrium in solution, since the equilibrium is almost instantaneously established when the dimalonato salt is dissolved in malonate buffers, and the extinction coefficient of the trimalonato ion may be calculated from the measured extinction in suitable mixtures.

We have attempted to make mixed hexa-acido complexes by replacing the two water molecules of the dimalonato salt by an oxalate ion, according to the reaction

$$[Mn(C_3H_2O_4)_2(H_2O)_2]^- + C_2O_4^{--} \longrightarrow [Mn(C_3H_2O_4)_2(C_2O_4)]^{---} + 2H_2O$$

When stoichiometric quantities are mixed with very little water, a portion of the dimalonato salt is converted into the **trioxalato salt,** while the rest remains undissolved. Oxalic acid in excess gives the green isomer of the dioxalato compound. An oxalate buffer in sufficient quantity converts the dimalonato salt into the trioxalato compound with good yield.

Equilibrium between the Di- and Trimalonato Ions.—Addition of potassium malonate to an acid solution of the dimalonato complex produces a color change which is reversed by dilution or by addition of more acid. The red color is due to the shift of the reaction toward the trimalonato ion, and we have determined the equilibrium constant of the reaction by spectrophotometric analysis of the solutions. The general procedure was similar to that used in the oxalato equilibrium by Cartledge and Ericks[1] (second paper), although in the malonato experiments all solutions were necessarily prepared from the dimalonato complex, and simple aqueous solutions could not be used because of their instability. Furthermore, in order to reduce irregularities due to the uncertain activity coefficients, all solutions were brought to a constant ionic strength of 0.265 by addition of potassium nitrate, if necessary. The equilibrium constant refers to the reaction

$$[Mn(C_3H_2O_4)_3]^{---} + 2H_2O \rightleftarrows [Mn(C_3H_2O_4)_2(H_2O)_2]^- + C_3H_2O_4^{--}$$

The equilibrium constant determined is given by the equation

$$\frac{\gamma_1\gamma_2}{\gamma_3}\,\frac{[Mn(C_3H_2O_4)_2(H_2O)_2^-][C_3H_2O_4^{--}]}{[Mn(C_3H_2O_4)_3^{---}]} = K$$

in which the gammas are the activity coefficients of the ions with the valence corresponding to the subscript. These activity coefficients were estimated as in the previous work (1, second paper) and are included in the value of the equilibrium constant finally calculated. The various equilibrium mixtures were prepared at 0° and quickly analyzed spectrophotometrically as previously described. There was no perceptible decomposition in the short time required for the measurements. The solutions were prepared by adding pure potassium dimalonatodiaquomanganiate to standard malonic acid or malonate buffers.

If E is the apparent molecular extinction coefficient of any mixture calculated from its measured transmittance, E_1 and E_3 are the molecular extinction coefficients of the dimalonato and trimalonato ions, respectively, c_0 is the concentration of malonate ions in the buffer itself, and c is the formality of the manganiate complex, we have

$$\frac{\gamma_1\gamma_2}{\gamma_3}\left(\frac{E_3 - E}{E - E_1}\right)\left[c_0 - \left(\frac{E - E_1}{E_3 - E_1}\right)c\right] = K$$

The extinction coefficient of the dimalonato ion was directly determined on solutions of the complex in 0.05 M malonic acid. In order to find E_3, the molecular extinction coefficient of the trimalonato ion, we prepared pairs of buffers of known malonate-ion concentration and of equal formality in complex. From the absorption measurements on each such pair the approximate value of E_3 was calculated by omission of the small term containing c in the equation above. By addition of potassium nitrate to the more dilute solutions, the ionic strength was kept at a value of 0.265, in order that the activity-coefficient term might be cancelled in calculating E_3. The approximate values of E_3 were then used in the last term of the equation above to obtain more exact values of E_3. From the average value of E_3 obtained from four solutions and for five wave lengths the equilibrium constant was calculated, the activity coefficients being estimated as described in the previous work. Only the final values of E_3 are given in the tabulation below; the approximate values differed from these by hardly more than the probable error in measurement.

TABLE I

MEASURED APPARENT EXTINCTION COEFFICIENTS (COMPLEX 0.005 FORMAL)

	Solvent formality		Wave length, mμ				
	$K_2C_3H_2O_4$	$KHC_3H_2O_4$	510	520	530	540	560
(a)	0.08	0.02	125	109	94	79	54
(b)	.04	.01	100	84	70	58	39
(c)	.06	.02	112	99	83	70	48
(d)	.03	.01	91	77	62	51	34

The final calculated values of E_3 and the measured value of E_1 were as follows

Wave length, mμ	510	520	530	540	560
E_3	217	197	180	153	115
E_1	59	42	29	21	13

The values taken for the activity coefficients were: $\gamma_1 = 0.44$; $\gamma_2 = 0.17$; $\gamma_3 = 0.14$. Table II gives a summary of the equilibrium constants found for the four buffers shown in Table I, each solution being measured at five wave lengths.

TABLE II

CALCULATED EQUILIBRIUM CONSTANTS

Buffer	Wave length, mμ				
	510	520	530	540	560
(a)	0.058	0.055	0.055	0.053	0.062
(b)	.059	.053	.056	.053	.060
(c)	.062	.053	.056	.052	.060
(d)	.061	.056	.055	.053	.060

Average, $K = 0.057$, 0°

The value previously reported for the corresponding oxalato equilibrium constant is 0.0038 at 0°. For the reactions as written, the free-energy changes are as follows:

Malonato ions: $\Delta F^\circ_{273} = 1550$ cal.
Oxalato ions: $\Delta F^\circ_{273} = 3020$ cal.

These data show that the third anion is rather loosely bound in both cases, but more loosely in the malonate than in the oxalate. . This instability of the trimalonato ion readily accounts for the difficulty in isolating pure salts of this type, since, in a 0.1 *M* solution, replacement of the third malonate ion by water molecules may be calculated to occur to the extent of about 52%. This is sufficient to exceed the solubility product of the dimalonato salt by a factor of three. At the same concentration, the trioxalato complex is only about 18% converted and is readily isolable.

Electrode Potential Measurements.—As a preliminary to an extended study of the electrode potentials in systems including manganic complexes, we prepared cells consisting of a normal calomel half-cell and a manganous–manganic half-cell. The latter contained manganous sulfate (0.005 *M*) and the dioxalato or dimalonato manganiate (0.005 *M*) in the corresponding free acid (0.1 *M*); the electrode was a platinum spiral. The calomel electrode was at room temperature, while the complex solution was at 0°. The electromotive force was measured with a Type K potentiometer (Leeds and Northrup). From the measured e. m. f. the standard potential was calculated for the reaction

$$Mn^{++} + 2X^{--} + 2H_2O \rightleftharpoons [MnX_2(H_2O)_2]^- + \epsilon$$

Activity coefficients were obtained by the interpolation methods previously mentioned, except that the activities of the malonate and oxalate ions in the acid solutions were set equal to their respective thermodynamic secondary ionization constants as an approximation. The details of the calculations will be given more fully in a subsequent paper.

Owing to the instability of the solutions even at 0° an error of a few millivolts is unavoidable. The measurements consistently showed, however, that the standard potential in the oxalic acid solution corresponds to a lower concentration of manganic ions by about 0.040 volt.

Summary

1. We have described the preparation and properties of hydrated and anhydrous forms of potassium dimalonatomanganiate.

2. We have determined the easy conversion of this complex into other anion complexes containing phosphoric acid, cyanide, catechol, salicylate, or cupferron.

3. We have analyzed spectrophotometrically solutions of the complex in various malonate buffers and calculated the equilibrium constant for the reaction

$$[Mn(C_3H_2O_4)_3]^{---} + 2H_2O \rightleftharpoons [Mn(C_3H_2O_4)_2(H_2O)_2]^- + C_3H_2O_4^{--}$$

The value is 0.057 at 0°, corresponding to a standard free energy change $\Delta F^\circ_{273} = 1550$ cal.

4. Preliminary measurements of electrode potentials indicate that the dioxalatodiaquo complex is more stable than the dimalonato complex by somewhat less than 1000 cal. per mole.

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