Summary

1. A procedure has been developed whereby potassium trioxalatomanganiate may be prepared spectroscopically free from iron.

2. Potassium dioxalatodiaquomanganiate has been prepared in the pure crystalline state. Two forms of the trihydrate have been obtained, as well as the anhydrous salt.

3. It has been shown that these manganiate ions form sparingly soluble salts with complex cations.

4. Pure potassium dimalonatodiaquomanganiate has been prepared and certain of its properties have been determined.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF BUFFALO]

Equilibrium between the Trioxalatomanganiate and Dioxalatodiaquomanganiate Ions

BY G. H. CARTLEDGE AND W. P. ERICKS

In spite of the enormous number of transformations among complex compounds that have been developed in the course of the classic researches of Werner and his successors, very few of such reactions have been investigated quantitatively from the standpoint of chemical equilibrium. The complexes of the metals that have been most fully studied are, as a rule, so stable with respect to dissociation that readily measurable equilibria are comparatively rare. Such measurements as have been made concern principally the dissociation of solid ammine complexes or the instability constants of such relatively stable complexes as the silver–ammonia or silver–cyanide ions in solution. In a few cases the acidic dissociation of aquo complex ions has also been studied.[1] Investigations of affinity in the complex compounds are desirable on account of the renewed interest in the question as to the type and strength of the chemical bonds in such substances.

Meyer and Schramm[2] observed that the trioxalatomanganiate ion and the dioxalatodiaquomanganiate ion are convertible one into the other according to the equation

$$[Mn(C_2O_4)_3]^{\equiv} + 2H_2O \rightleftarrows [Mn(C_2O_4)_2(H_2O)_2]^- + C_2O_4^=$$

That a measurable equilibrium is established rapidly is evident from the color changes observed in aqueous solutions of the trioxalatomanganiates. A concentrated aqueous solution is ordinarily described as cherry-red. We have found that the color is perceptibly changed to a more purplish-red upon addition of an oxalate–oxalic acid buffer at *p*H 4.5. As an aqueous solution is diluted its color changes steadily; in 0.001 *M* solution the color is brown, but may be restored to red by addition of an excess of the oxalate buffer. The dioxalatodiaquomanganiate ion reacts immediately with the oxalate ion to produce the trioxalato complex. In this respect the dioxalato ion contrasts with the dimalonato ion, which is very incompletely converted to the trimalonato ion. The dioxalatodiaquomanganiate ion itself has a golden-yellow color in cold aqueous solution, but the solution is acid and soon becomes turbid. This effect is no doubt due to an acidic ionization of the water molecules in the complex, whereby a sparingly soluble hydroxo complex is formed. We have found that the solution in 0.01 *M* nitric acid remains clear and is stable enough for our purposes. The nitric acid evidently suppresses the ionization, giving the pure color of the aquo complex ion.

The method of determining the equilibrium concentrations consisted in a spectrophotometric analysis of solutions of the trioxalatomanganiate in water at various concentrations and also in various oxalate–oxalic acid buffer mixtures. Equilibrium was also approached from the dioxalatodiaquomanganiate side of the reaction. As has been found by Uspensky and his collaborators[3] in a number of cobaltic and chromic complexes, when water molecules replace an acido group within a complex ion the maximum absorption in the visible region is displaced in the direction of shorter wave lengths. In the oxalatomanganiates

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[1] Brönsted and King, *Z. physik. Chem.*, **130**, 699 (1927).

[2] Meyer and Schramm, *Z. anorg. allgem. Chem.*, **157**, 190 (1926).

[3] Uspensky and others, *Trans. Inst. Pure Chem. Reagents, U. S. S. R.*, **13**, 1 (1933).

the same shift is observed, and is so great as to permit convenient determination of the ions in a mixture. The calculation of the concentrations depends upon a knowledge of the extinction coefficients of the pure components. In the case of the dioxalatodiaquomanganiate the extinction coefficient is relatively small in the region of most importance for our measurements. Furthermore, the values differ only slightly whether the salt is dissolved in pure water, in dilute oxalic acid or in dilute (0.01 N) nitric acid. We have therefore taken the measurements on this salt in 0.01 N nitric acid, since this concentration was found ample to prevent dissociation to a hydroxo complex; at 0° the solution does not decompose rapidly enough to interfere with the analysis.

In the case of the trioxalatomanganiate it was found that there is an appreciable replacement of an oxalate ion by water molecules even in the most favorable oxalate buffer. It is therefore impossible to determine the extinction coefficients for the pure component in these solutions. We have avoided this difficulty by making measurements at a low concentration of the complex in a pair of buffered solutions of known oxalate-ion concentration. By treating both the extinction coefficient of the trioxalato ion and the equilibrium constant as unknowns we arrive at pairs of equilibrium equations from which both quantities may be calculated. The extinction coefficients thus found at three wave lengths were then used for other solutions in which the oxalate-ion concentration was not necessarily known.

For the calculation of the concentration of the components in the equilibrium mixture the Lambert–Beer law was used in the form

$$\log (I_0/I) = lc(x_1E_1 + x_3E_3) \qquad (1)$$

in which c is the formality as to manganese, l the cell length in cm., x_1 and x_3 the fractions of the complex in the form, respectively, of the univalent dioxalato ion and the tervalent trioxalato ion, and E_1 and E_3 the molecular extinction coefficients of the corresponding ions. If the apparent extinction coefficient calculated from the measured transmittance of any mixture is E, we obtain

$$E = x_1E_1 + x_3E_3 \qquad (2)$$

The fractions of the complex in the two forms are then given by

$$x_1 = (E_3 - E)/(E_3 - E_1) \text{ and } x_3 = (E - E_1)/(E_3 - E_1) \qquad (3)$$

The extinction coefficients were measured from 440 mμ to 600 mμ in certain cases, but the three wave lengths 550, 540 and 520 mμ were selected for the equilibrium calculations. The extinction coefficients at these points were then repeatedly determined on freshly prepared solutions. A Bausch and Lomb visual spectrophotometer was used, the cells being jacketed in ice during the measurements. A jet of dry air prevented the condensation of moisture on the cells. The least stable solutions showed no alteration during the few minutes they were in use. Distilled water boiled in quartz was used for preparing the unbuffered solutions. All salts used were pure, as determined from careful analyses.

For the equilibrium equation we have

$$\frac{\gamma_1[\mathrm{Mn(C_2O_4)_2(H_2O)_2}^-]\gamma_2\mathrm{C_2O_4}^{=}]}{\gamma_3[\mathrm{Mn(C_2O_4)_3}]^{\equiv}} = K \qquad (4)$$

the γ's being the activity coefficients of the respective ions. Expressed in terms of the fractions of the two colored ions this becomes

$$\frac{\gamma_1\gamma_2}{\gamma_3} \times \frac{x_1}{1 - x_1} \times [\mathrm{C_2O_4}^{=}] = K \qquad (5)$$

The values of the activity coefficients were obtained from graphs of the coefficients of the chlorate, sulfate and ferricyanide ions. For the univalent ion the activity coefficient was plotted against the cube root of the ionic strength. In the case of the bivalent and tervalent ions the reciprocal of the activity coefficient was plotted against the square root of the ionic strength. Taking the numerical values from Lewis and Randall,[4] essentially linear graphs were obtained from which the required activity coefficients could be read with only moderate extrapolation to the more concentrated mixtures. In calculating the oxalate-ion concentration in the buffered solutions due regard was paid to the secondary ionization of oxalic acid in all cases where required. In terms of the individual extinction coefficients the equilibrium equation takes the form

$$\frac{\gamma_1\gamma_2}{\gamma_3}\left(\frac{E_3 - E}{E - E_1}\right)\left[c_0 + \left(\frac{E_3 - E}{E_3 - E_1}\right)c\right] = K \qquad (6)$$

when equilibrium is approached from the trioxalato side; c_0 is the concentration of oxalate ions in the buffer solution itself.

In making the calculations different values were employed for the extinction coefficient E_1 of the dioxalatodiaquomanganiate ion depending upon the acidity of the solution. In the acidic, buffered solutions the values were taken from measurements on the pure component in 0.01 N nitric acid as the solvent. In the more nearly neutral,

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[4] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, N. Y., 1923, p. 382.

unbuffered solutions the values obtained from a simple aqueous solution of the dioxalato salt were used, as these undoubtedly represent more closely the actual state of the substance in the equilibrium mixtures. Owing to the unavoidable uncertainty in these extinction coefficients, however, we have selected wave lengths at which the values are still relatively small in comparison with those of the trioxalato ion.

The values of the extinction coefficients of the trioxalato ion were first determined approximately from measurements on a 0.001 *M* solution of the complex in buffers consisting of 0.08 *M* potassium oxalate and 0.02 *M* potassium hydrogen oxalate, KHC_2O_4, in one case, and the same buffer diluted with an equal volume of water in the second case. In these buffers the oxalate ion contributed by the reaction of the complex ion with water is negligibly small. From the approximate results so obtained final values for the extinction coefficients of the trioxalato ion were then obtained from three series of measurements in buffers containing 0.02 *M* potassium oxalate and 0.08 *M* potassium hydrogen oxalate, or the same diluted with an equal volume of water. The approximate values of the extinction coefficients E_3 previously obtained made it possible to calculate with sufficient accuracy the amount of oxalate ion formed in the reaction. The replacement reaction proceeds further in these more acidic buffers, and the calculated extinction coefficients are consequently less sensitive to errors in the measurements.

TABLE I

CALCULATED EXTINCTION COEFFICIENTS OF THE TRIOXALATOMANGANIATE ION

Expt.	Wave lengths, mμ 550	540	520
3, 4	232	274	303
12, 13	248	276	314
16, 17	237	266	306
Average E_3	239	272	308

For the determination of the extinction coefficients of the trioxalatomanganiate ion experiments 3, 4, 12, 13, 16 and 17 (Table II) were used. The results are summarized in Table I.

The general results and calculated equilibrium constants in buffered and aqueous solutions are shown in Table II. Certain of the measured extinction coefficients are shown in Fig. 1.

Discussion of Results

From Table II it will be seen that in different experiments we have carried the replacement reaction from 10–70% toward completion in the solutions containing added oxalate ions. In simple aqueous solution the range was from 31–85%. Equilibrium has been approached from both sides, and it is evident that the reaction proceeds to equilibrium almost instantaneously, since the absorption measurements were started

TABLE II

COMPOSITION OF EQUILIBRIUM MIXTURES AND CALCULATED EQUILIBRIUM CONSTANTS

Expt.	Solute and formality, *c*	Solvent formality $K_2C_2O_4$	KHC_2O_4	Fraction as dioxalato ion, x_1	*K*, calcd. $\times 10^3$
1	$K_3[Mn(C_2O_4)_3]$, 0.001 *M*	0.08	0.02	0.096	5.0
2	$K_3[Mn(C_2O_4)_3]$, .001 *M*	.04	.01	.126	4.1
3	$K_3[Mn(C_2O_4)_3]$, .001 *M*	.02	.08	.159	3.0
4	$K_3[Mn(C_2O_4)_3]$, .001 *M*	.01	.04	.233	2.8
5	$K_3[Mn(C_2O_4)_3]$, .002 *M*	.08	.02	.096	5.0
6	$K_3[Mn(C_2O_4)_3]$, .002 *M*	.04	.01	.134	4.4
7	$K_3[Mn(C_2O_4)_3]$, .002 *M*	.0016	.0004	.597	3.8
8	$K_3[Mn(C_2O_4)_3]$, .001 *M*	.0008	.0002	.702	3.5
9	$K_3[Mn(C_2O_4)_3]$, .005 *M*	.0008	.0002	.568	4.1
10	$K_3[Mn(C_2O_4)_3]$, .01 *M*	.08	.02	.095	4.6
11	$K_3[Mn(C_2O_4)_3]$, .01 *M*	.04	.01	.099	3.2
12	$K_3[Mn(C_2O_4)_3]$, .01 *M*	.02	.08	.134	2.2
13	$K_3[Mn(C_2O_4)_3]$, .01 *M*	.01	.04	.197	2.3
14	$K[Mn(C_2O_4)_2(H_2O)_2]$, 0.001 *M*	.08	.02	.094	4.8
15	$K[Mn(C_2O_4)_2(H_2O)_2]$, .001 *M*	.04	.01	.145	4.7
16	$K[Mn(C_2O_4)_2(H_2O)_2]$, .001 *M*	.02	.08	.176	3.1
17	$K[Mn(C_2O_4)_2(H_2O)_2]$, .001 *M*	.01	.04	.274	3.1
18	$K_3[Mn(C_2O_4)_3]$, 0.001 *M*	.00	.00	.845	4.6
19	$K_3[Mn(C_2O_4)_3]$, .002 *M*	.00	.00	.728	3.8
20	$K_3[Mn(C_2O_4)_3]$, .010 *M*	.00	.00	.499	4.4
21	$K_3[Mn(C_2O_4)_3]$, .025 *M*	.00	.00	.309	2.4
					Average 3.8

as quickly as possible after the preparation of the solution. The range of concentrations as to the complex salt is necessarily restricted by the intensity of the absorption, but we have covered as wide a range as could be measured with any degree of precision with the visual spectrophotometer, namely, from 0.001 to 0.025 *M*. Considering the instability of the system, the necessity of approximating the activity coefficients, and the inherent difficulties in the precise determination of the extinction coefficients, the concordance of the equilibrium constants is all that could be expected.

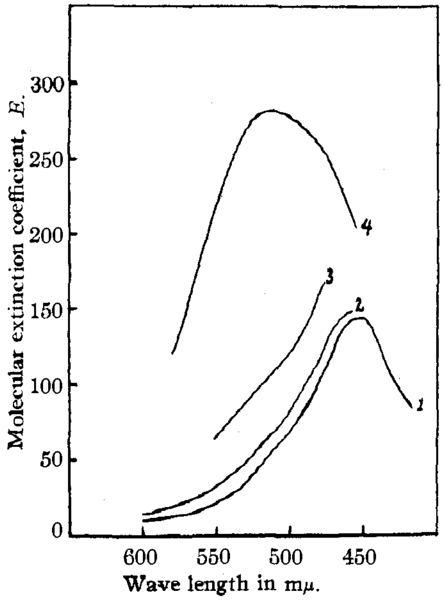

Fig. 1.—Absorption spectra: curve 1, $K[Mn(C_2O_4)_2(H_2O)_2]$, 0.01 *M* in 0.01 *M* HNO_3; curve 2, $K[Mn(C_2O_4)_2(H_2O)_2]$, 0.01 *M* in water; curve 3, $K_3[Mn(C_2O_4)_3]$, 0.001 *M* in water; curve 4, $K_3[Mn(C_2O_4)_3]$, 0.01 *M* in buffer 0.08 *M* in $K_2C_2O_4$ and 0.02 *M* in KHC_2O_4.

The absence of any trend in the calculated constants as the replacement reaction becomes extensive shows that under the prevailing conditions the dioxalato ion does not lose a second oxalate ion to an appreciable extent. The dioxalato ion may be decomposed by addition of ions that form very insoluble oxalates, but it is evident that such a reaction proceeds only at decidedly lower concentrations of oxalate ions than were present even in our most dilute solutions. The ready loss of one oxalate ion from the trioxalatomanganiate ion contrasts strongly with the behavior of the trioxalato chromiates and cobaltiates, which are not decomposed even by addition of cations which form very insoluble oxalates.

Figure 1 shows the extinction coefficients of certain of the systems measured. In the case of the dioxalatodiaquomanganiate the same absorption was observed whether the green or the yellow form of the salt was used.[5] Either form of the salt is converted immediately to the trioxalato complex by addition of potassium oxalate. When preparing the dioxalato complex we have sometimes isolated both kinds of crystals from the same solution. These results appear to indicate that in aqueous solution there is an equilibrium between the yellow and green forms, which we assume to be *cis* and *trans* isomers.

The maximum absorption of the dioxalato complex lies at about 450 mμ, whereas that of the trioxalato salt is at about 520 mμ. This shift of 70 mμ is in the same direction as observed by Uspensky and collaborators,[3] but is considerably greater in magnitude. The Russian authors have also observed that in the case of *cis-trans* isomers the *trans* isomer often has an absorption minimum at approximately the same wave length at which the *cis* isomer has a maximum. This rule was found to hold for a number of chromium and cobalt complexes, and if it applies to the manganese compounds it would indicate that our yellow dioxalato salt is the *cis* isomer. That this form predominates to such a large extent in aqueous solution is in accordance with the statistical probability, which, for the *cis* isomer, is 0.8 in such a case.

The magnetic susceptibility of potassium trioxalatomanganiate has been determined by Johnson and Mead[6] and found to correspond to four unpaired electrons. These authors therefore concluded that the complex must be held together by ionic bonds, since if there were six covalent bonds there would be only two unpaired electrons. Another possibility has to be considered, however. According to Pauling's rules for the covalent bonds in complex ions[7] tervalent manganese in its normal state should have four unpaired electrons and just the combination of available *d*, *s* and *p* eigenfunctions required for the formation of four covalent bonds directed toward the corners of a square. The readiness with which the trioxalatomanganiate ion loses its first oxalate ion, and the abnormally large shift in the absorption

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(5) Cartledge and Ericks, This Journal, **58**, 2061 (1936).

(6) Johnson and Mead, *Trans. Faraday Soc.*, [5] **29**, 626 (1933).

(7) Pauling, This Journal, **53**, 1367 (1931).

maximum when this occurs, suggest the hypothesis that two of the oxalate ions are covalently bound, while the third is held by the weaker ionic forces. Such a structure would agree with the observed magnetic susceptibility. Further work is in progress in an attempt to gain more insight into the structure of these complexes.

Summary

1. The extinction coefficients of aqueous and buffered solutions of potassium trioxalatomanganiate and potassium dioxalatodiaquomanganiate at various concentrations have been measured in the visible region of the spectrum. The trioxalato salt has a maximum absorption at about 520 mμ and the dioxalato salt at about 450 mμ.

2. The two salts are convertible into each other according to the reaction

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

Equilibrium is established almost instantaneously. The equilibrium constant of the reaction has been determined by spectrophotometric analysis and found to be 3.8×10^{-3} at 0°.

3. The green and yellow dioxalato salts both give a golden-yellow solution with the same absorption curve, and the solution presumably consists of an equilibrium mixture of the two isomers. The optical evidence makes it likely that the yellow form is the statistically more probable *cis* isomer.

4. It is suggested that the complex manganiates may be derived from a covalent dsp^2 structure fundamentally, the fifth and sixth valence bonds being ionic or ion-dipole in character.

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An Oxalato Complex of Quadrivalent Manganese

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In the course of the investigation described in a previous paper[1] an attempt was made to prepare a hydroxo-oxalato complex compound containing tervalent manganese. In the previous experiments on the trioxalatomanganiate potassium permanganate was first reduced all the way to the manganous state by an excess of oxalic acid; the manganous ion was then oxidized by addition of a second portion of permanganate, the exact product being determined by the proportions of the reactants used. In view of the weakly acidic character of the water molecules in the dioxalatodiaquomanganiate ion, it was thought that the corresponding hydroxo ion might be obtained by suitable decrease of the hydrogen-ion concentration. Accordingly, a preparation was carried out in which part of the oxalic acid was replaced by potassium oxalate, using the proportions:

$$3.5H_2C_2O_4 : 0.5\ K_2C_2O_4 : KMnO_4$$

The materials were allowed to react at a little above 0° and the result was a mixture of two kinds of crystals. Microscopic examination showed the presence of some potassium trioxalatomanganiate along with a considerably larger proportion of dark, olive-green crystals. The experiment was repeated with further alteration in the reacting proportions until a method was finally developed which gave the green material in pure form. Although the substance is very unstable we were able to isolate it and prove that it contains quadrivalent manganese, its composition being represented accurately by the formula $K_2[Mn^{IV}(C_2O_4)_2(OH)_2]\cdot 2H_2O$. It is therefore to be called potassium dioxalatodihydroxomanganeate. So far as we have been able to discover it is the only known complex of quadrivalent manganese with the exception of the hexahalogenato complexes $[MnX_6]^{2-}$ and a diglycerol complex reported by Schottländer.[2]

Preparation.—The preparation is conducted according to the reaction

$$3.5H_2C_2O_4 + 0.65K_2C_2O_4 + KMnO_4 \longrightarrow K_2[Mn(C_2O_4)_2(OH)_2] + 0.5H_2C_2O_4 + 0.15K_2C_2O_4 + 3CO_2 + 2H_2O$$

The operations are conducted rapidly, in a cool and darkened room. Fourteen hundredths of a mole of oxalic acid (17.64 g. $H_2C_2O_4\cdot 2H_2O$) is dissolved in 250 cc. of distilled water. The solution is cooled to 0° and 0.04 mole (6.32 g.) of powdered potassium permanganate is added, followed by 0.026 mole of potassium oxalate (4.78 g. $K_2C_2O_4\cdot H_2O$). The mixture is agitated vigorously for about twenty minutes and the temperature is allowed to rise to 7°. At this point carbon dioxide begins to be

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

[2] Schottländer, *Ann.*, **155**, 230 (1870).