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Kinetics of the Periodate Oxidation of Manganese to Permanganate[1]

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The kinetics for the oxidation of manganese by periodate were studied by a spectrophotometric method. Oxidation of manganese(II) was found to be autocatalytic. The rate dependence for the formation of permanganate was first order in both manganese(II) and periodate and half order in permanganate. The dependence on perchloric acid concentration was complex, and the observed rates passed through a minimum. In concentrated iodic acid solutions an appreciable quantity of an iodate complex of manganese(III) was formed, in which case the rate dependence approached first order in the complex and second order in periodate. Some other properties of the manganese(III)–iodate complex were reported. A mechanism for the oxidation has been proposed to explain the rate dependences as well as other effects observed.

Introduction

A kinetic study of the oxidation of manganese to permanganate by periodate has been carried out at room temperature. This reaction

$$2Mn^{++} + 5IO_4^- + 3H_2O \longrightarrow 2MnO_4^- + 5IO_3^- + 6H^+ \quad (1)$$

is used in a familiar colorimetric determination for manganese. The work has been directed toward the establishment of a rate expression and the development of a mechanism to explain the observed rates. For such a complex reaction an acceptable mechanism must describe a number of simple steps, each capable of occurring in sequence with a satisfactory rate. Since intermediate oxidation states must react in some of the steps, the kinetics may provide important information about these states which at present have been incompletely described.

Recently, quantitative work on the kinetics of this reaction was reported by Strictland and Spicer.[2] Their experiments were carried out at temperatures above 60°. They showed that the reaction was autocatalytic and that the rate of permanganate formation was increased by the presence of manganese dioxide and by an increase in ionic strength.

Experimental

Materials.—Periodic acid, iodic acid and potassium hydrogen iodate of reagent quality, supplied by the G. Frederick Smith Co., were used in these studies. The potassium hydrogen iodate served as a primary standard for acidimetric and iodometric titrations. The purities of the other reagents were tested and their solutions standardized by conventional analytical methods. Dilute potassium permanganate solutions were prepared by dissolving crystals, heating and filtering several times through sintered glass disks. The perchloric acid used was of reagent grade. Manganese(II) perchlorate was prepared by dissolving very pure electrolytic metal in a minimum amount of perchloric acid and diluting.

Upon testing some of the kinetic variables, it became apparent that an iodate complex of manganese(III) with a violet color was formed. This complex has warranted further investigations and is being studied currently. Results of this work will be reported separately. To obtain a solution with this complex, manganese(II) iodate was added to iodic acid solution. Potassium permanganate solution was then added slowly in an amount which was not sufficient to give complete oxidation of all the manganese(II) to manganese(III). The resulting pale violet solution was filtered through sintered glass to remove the excess solid manganese(II) iodate. By this method it was easily possible to obtain solutions containing about 10^{-3} molar total manganese in 1 molar iodic acid. The twin maxima, characteristic of the permanganate absorption spectrum, were not detectable in these solutions. A single absorption peak fell in the same wave length region as the permanganate peaks; however, the extinction coefficient of the complex at 5260 Å. was about 5% of the permanganate value. In some cases additional permanganate was added to oxidize the manganese(II) remaining from the equilibrium with the solid.

Procedure.—The course of the reaction was followed by measuring the absorption of light in a Cary recording spectrophotometer, Model 12. The intense color of the permanganate ion lent itself admirably to these measurements. The absorption maximum at 5260 Å. gave an extinction coefficient of 2240 moles^{-1} liter cm.$^{-1}$ on this instrument. Interference by solutions of perchloric acid, periodic acid, iodic acid and manganese(II) at this wave length was negligible. Two types of measurements were employed. In one, the wave length scanning mechanism was locked at 5260 Å. The Cary Instrument plotted the optical density, defined in this paper as log (I_0/I), as a function of time. This quantity was essentially proportional to the permanganate concentration since the absorption by all other ionic species was small. In the other method the spectrum from 3600 to 7000 Å. could be scanned at 3-minute intervals.

Quartz cells with a path length of 1.00 cm. and a volume of 2.91 ml. were used for the reaction vessels. Copper tanks with water were placed adjacent to the cells to serve as thermal ballast. During a given set of experiments the temperature remained constant to within ±0.2°. Most measurements were made at the ambient cell chamber temperature of 28°. Reagents were stored at this temperature before the cell was filled.

Each of a number of initial concentration variables was tested by a series of runs. Periodic acid and perchloric acid were always present in such an excess that their concentration and therefore the ionic strength and *p*H of a solution did not change appreciably during a reaction. Manganese(II) and permanganate were variables which could not be treated in this fashion because of the high extinction coefficient of the permanganate. The reaction was also followed in solutions in which the initial iodate content was zero, in which the initial iodate (3.88×10^{-3} *M*) was about twice as great as the iodate formed by complete reaction and in which the iodate was present in great excess (0.5 *M*).

Solutions of the various standardized reagents were transferred to the absorption cell by calibrated micropipets. The manganese(II) or manganese(III) solutions were added last. The cell was stoppered, shaken and transferred to the spectrophotometer. The time interval from shaking until the instrument was recording was from 10–20 seconds as indicated by a stop watch.

Results and Discussion

The starting concentrations used to ascertain the kinetics variables of this reaction are listed in Table I. In Fig. 1, a series of the spectrophotometer plots obtained during the course of typical reactions have been presented to illustrate the sigmoid character of the curves and also to indicate the relative effect of some of the concentration variables. The inflection of these curves indicates that the reaction mechanism is complex. Either a considerable fraction of manganese must be stored in some intermediate oxidation state, or rapid oxidation requires an interaction between the products and the reactants, *i.e.*, autocatalysis. (In this paper the time from the starting of the reaction to the inflection point is called the induction period.)

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[1] Work was performed in the Ames Laboratory of the Atomic Energy Commission.

[2] J. D. H. Strictland and G. Spicer, *Analytica Chimica Acta*, **3**, 517 (1949).

TABLE I

INITIAL CONCENTRATIONS AND MAXIMUM OBSERVED RATES FOR THE OXIDATION OF MANGANESE(II) AT 28°

$[HClO_4]$[a]	$[H_5IO_6]$	$10^4 \times [Mn(ClO_4)_2]$	$10^3 \times [KH(IO_3)_2]$	$10^5 \times [KMnO_4]$	Maximum rate (d[O.D.]/dt)max.[b]
0.478	0.250	3.54			0.126
.974	.250	3.54			.120
.990	.250	3.54			.113
1.923	.250	3.54			.104
2.94	.250	3.54			.104
3.78	.250	3.54			.116
1.885	.500	3.54			.196
1.885	.312	3.54			.132
1.885	.250	3.54			.122
1.885	.187	3.54			.081
1.885	.125	3.54			.050
0.424	.167	3.12	1.94		.061
.424	.167	3.92	1.94		.088
.424	.167	6.20	1.94		.178
.424	.167	7.81	1.94		.22
.424	.144	3.12	1.94	0	.049
.424	.144	3.12	1.94	3.02	.058
.424	.144	3.12	1.94	6.05	.065
.424	.144	3.12	1.94	12.1	.075
.424	.144	3.12	1.94	30.2	.106
.424	.144	3.12	1.94	60.5	.116
.424	.144	3.12	1.94	90.6	.136

[a] All concentrations are given in moles/liter. [b] This quantity has been set equal to 2240 d$[MnO_4^-]$/d*t* moles liters^{-1} min.$^{-1}$.

Manganese(III) Oxidation.—Curve F in Fig. 1 illustrates the course of oxidation of the iodate complex of manganese(III) by periodate in 0.5 *M* iodic acid. It can be seen from the curve that the induction period was very nearly although not completely eliminated. When the log (O.D.$_{max}$ − O.D.) *vs.* the time was plotted, the curves fell accurately along a straight line for the last 80% of the reaction. Conditions used for testing the reaction orders are listed in Table II. The maximum optical density of the reaction mixtures with no initial permanganate corresponded to a permanganate concentration of about 80% of the total manganese. The solutions formed were not stable, however, and after a few hours a decrease in the optical density could be detected. In 24 hours the optical density fell to about 50% of its maximum value. Solutions of permanganate, perchloric acid and periodic acid in 0.5 *M* iodic acid underwent a similar slow fading of color. Apparently, iodic acid in these concentrations slowly reduces a considerable fraction of permanganate to the manganese(IV) state and would reduce a portion of the permanganate following its formation by periodate.

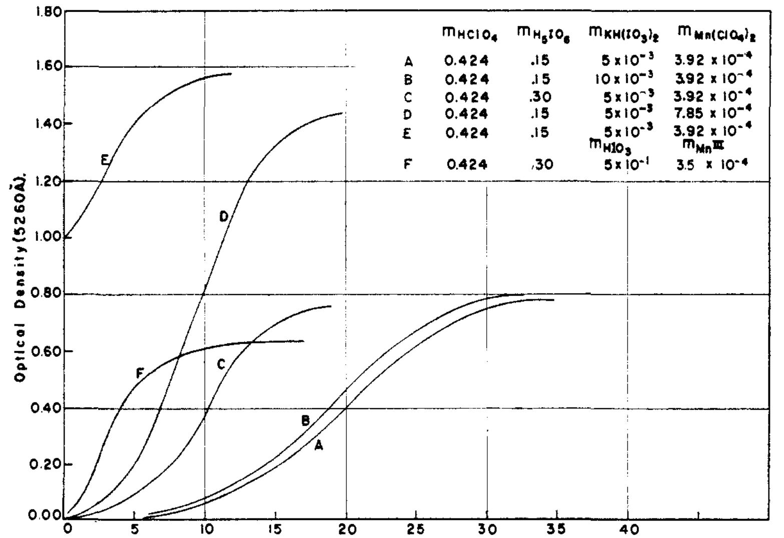

Fig. 1.—Typical optical density curves for the oxidation of Mn^{II} and Mn^{III} by periodic acid showing the relative effect of several concentration variables. Reaction mixture E originally contained 4.46 × 10⁻⁴ *M* $KMnO_4$.

Only the formation of permanganate occurring initially with a rapid rate, which is shown in curve F of Fig. 1, has been considered in this work. The quantity (O.D.$_{max}$ − O.D.) is proportional to the manganese which was still to form permanganate. Hence the linearity of the log(O.D.$_{max}$ − O.D.) *vs.* time plots indicated an oxidation which was first order in the manganese(III) complex. The slopes of the straight line portions are included in Table II, and it can be seen that they are independent of the initial manganese(III) concentration. When these slopes were plotted against the log $[H_5IO_6]$ in Fig. 2, it was found that the slope of the resulting curve approached a limit of 2.0 at high values of periodic acid, although it was somewhat smaller at low concentrations. This indicated a second-order reaction in periodic acid at high concentrations. In 0.5 *M* iodic acid the kinetics were described by the expression

$$D[MnO_4^-] = k[Mn^{III}][H_5IO_6]^2 \quad (2)$$

where *D* represents the operator d/d*t*, the brackets indicate molar concentrations, and $k \approx 3.0$ liters^2 moles^{-2} min.$^{-1}$ at 28°. Such a kinetics law suggests that the reaction involves a rapid equilibrium in which two periodate ions are added to the complex. Subsequently, the transfer of two oxygen atoms from periodate to manganese yields the products as indicated in the reactions

$$Mn^{III}(IO_3)_x^{3-x} + 2IO_4^- \rightleftarrows [Mn^{III}(IO_3)_y(IO_4)_2]^{1-y} + (x - y)IO_3^- \quad (3)$$

$$[Mn^{III}(IO_3)_y(IO_4)_2]^{1-y} + 2H_2O \longrightarrow MnO_4^- + (y + 2)IO_3^- + 4H^+ \quad (4)$$

The formation of such intermediate complexes by periodate has been proposed as a mechanism in some other oxidation reactions by Duke.[3] Experiments at 40° gave a temperature coefficient which indicated an experimental activation energy of approximately 17 kcal.

TABLE II

OXIDATION OF MANGANESE(III) SOLUTIONS AT 28°

Initial $[HClO_4]$ = 0.424*M*; initial $[HIO_3]$ = 0.500 *M*

Initial $10^4 [Mn^{III}]$[a]	Initial $10^4 [KMnO_4]$	Initial $[H_5IO_6]$	−d(log[O.D.$_{max}$ − O.D.])/d*t* Min.$^{-1}$
3.5	0	0.200	0.089
3.5	0	.300	.157
3.5	0	.400	.24
3.5	1.66	.400	.22
3.5	0	.500	.33
3.5	0	.600	.43
3.5	0	.700	.64
1.0	0	.300	.174
1.5	0	.300	.162
2.0	0	.300	.161

[a] Includes total manganese in the oxidation states II, III and IV.

The short induction period was believed to result from the manganese(II), originally in equilibrium with manganese(III) and manganese(IV)

$$Mn^{II} + Mn^{IV} \rightleftarrows 2Mn^{III} \quad (5)$$

Most of such manganese(II) would be oxidized by an initial

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[3] F. R. Duke, THIS JOURNAL, 69, 3054 (1947).

addition of permanganate. One manganese(III) solution in iodic acid was made 1.66 × 10^{-4} *M* in potassium permanganate before the addition of periodate. The log ($O.D._{max}$ − O.D.) curve was accurately straight for the complete reaction. The slope of this curve was, within the accuracy of the measurements, the same as the slope for the reaction in which all other variables were identical. In this particular case the permanganate formed corresponded to about 50% of the original manganese(III). This feature and also the other deviations from the rate expression 2 were consistent with the general mechanism discussed below to explain the manganese(II) data. The failure of permanganate to react rapidly with manganese(III) in this system is analogous to the case of the fluoride complex which can be formed by titrations to a permanganate color end-point.

Manganese(II) Reaction.—A consideration of the rate curves for manganese(II) illustrated by Fig. 1 indicated that permanganate was important in the oxidation. In cases for which no initial iodate was present, there would appear to be insufficient complexing agent present to store an appreciable fraction of manganese in the intermediate oxidation states.

A number of simple rate expressions were tried which would describe the course of a particular experiment for the complete reaction. These attempts were no more satisfactory than those of Strictland and Spicer[2] whose two parameter equations failed to describe the first 40% of the reaction. However, analyses of the sigmoid reaction curves were effected by measuring rates at the inflection points. These rates could be accurately measured since they changed only slowly over a considerable fraction of the reaction. In addition, the principal reaction processes contributed to the greatest extent at such points. These maximum rates are included with the data in Table I.

Features noted about the reactions have been listed below. (1) The initial presence of small amounts of iodate, *ca.* 5 × [Mn^{II}], produced only a minor increase in rate and decrease in induction period.

(2) The initial presence of permanganate greatly reduced the induction period. This behavior was enhanced by small quantities of iodate so that with the addition of both reagents the induction could be virtually eliminated.

(3) The addition of solid manganese dioxide accelerated the reaction. However, if manganese dioxide were not added, the absorption of the final solutions in certain visible wave length regions was very low and could be attributed to the permanganate spectrum alone. The solutions were all clear and gave no Tyndall effect; thus there was no evidence for the formation of a precipitate or colloid during the reaction.

(4) The rate was not strongly dependent on the perchloric acid concentration in the range of 0.4–4.0 molar, and it appeared to pass through a minimum at about 2 *M*. A part of this effect may have been due to the change in ionic strength which was reported to be a factor by Strictland and Spicer.[2] At somewhat lower acidities a red precipitate sometimes formed which was not MnO_2 but contained iodine and was similar to the material described by Price[4] and by Olsson.[5]

(5) Not all of the manganese was finally oxidized to permanganate. The final optical density was not a function of just the total manganese concentrations. Slower reactions usually gave higher yields. Reactions accelerated by increased iodate concentrations were an exception to this rule.

(6) The final spectrum indicated the presence of a manganese species other than permanganate which absorbed more highly at short wave lengths but did not interfere with the permanganate peaks.

(7) The temperature coefficient of the reaction over the range from 25–40° indicated an apparent activation energy of about 14 kcal.

The results in Table I represent four groups of experiments designed to show the dependence of the reaction rate on various concentration variables. In each group all but one of the initial concentrations were the same. When the perchloric acid concentration was constant, ionic strength and hydrogen ion concentration were effectively constant also. For the group with variable initial periodic acid concentration the maximum rate divided by the periodic acid was constant within the accuracy of the data. Hence the periodic acid dependence was first order.

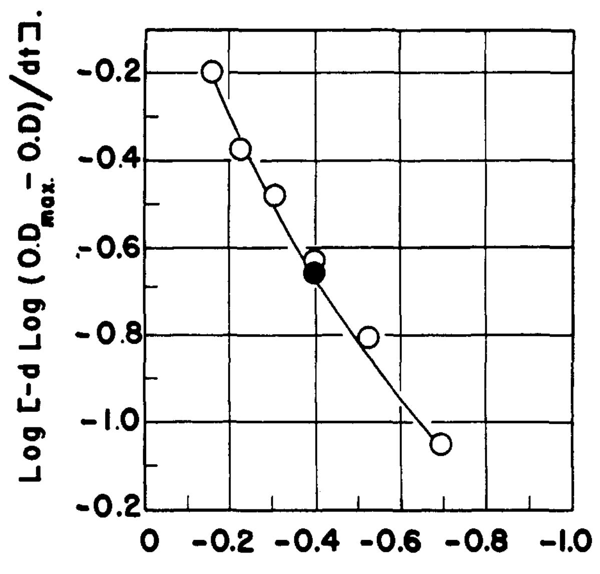

Fig. 2.—Log-log plot of the slopes, −d(log[$O.D._{max}$ − O.D.])/d*t*, against the periodic acid concentration for the oxidation of Mn^{III}.

To obtain the effect of permanganate, the maximum rate and the permanganate concentration at that instant, $[MnO_4^-]_{max}$, were taken from the optical density curves. From Table III it can be seen that the permanganate dependence was definitely of fractional order and seemed best described by an order of $^1/_2$.

TABLE III

DEPENDENCE OF THE MAXIMUM RATE FOR THE OXIDATION OF MANGANESE(II) UPON THE PERMANGANATE CONCENTRATION

(Calculated for experiments listed in Table I)

Initial $10^4 \times [MnO_4^-]$	$10^4 \times [MnO_4^-]^a_{max.}$	$(1/[MnO_4^-])^{1/2}$ $(d[O.D.]/dt)_{max.}$
0	1.20	4.5
0.302	1.34	5.0
0.605	1.55	5.2
1.21	1.83	5.5
3.02	3.77	5.5
6.05	6.52	4.5
9.06	9.48	4.4

^{a} Calculated from the optical density.

Quotients of the maximum rates divided by 1.5 power of the initial manganese(II) concentrations were also constant. However, the dependence upon permanganate must be factored out, so the dependence on the manganese(II) species was actually about first order.

The maximum rate at constant ionic strength in perchloric acid–dilute iodic acid solution is therefore given by the expression

$$D[MnO_4^-] = k[Mn^{II}][MnO_4^-]^{1/2}[H_5IO_6] \quad (6)$$

Mechanism.—A mechanism has been worked out to explain the observed details. The induction period, of course, indicates that periodate alone will not react rapidly with manganese(II). The permanganate dependence suggests that permanganate contributes to the oxidation of manganese(II) to give an intermediate state which does react with periodate. Manganese(III) iodate complex would be a logical choice for the intermediate state since its existence and behavior have been demonstrated. However, the Guyard reaction between

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(4) W. B. Price, *Am. Chem. J.*, **30**, 182 (1903).

(5) F. Olsson, *Arkiv. Kemi Mineral. Geol.*, **9**, No. 10, 5 (1924).

manganese(II) and permanganate to form manganese dioxide in perchloric acid solutions at concentrations comparable to the ones in this work also has an induction period. It follows that the reaction between manganese(II) and permanganate is also slow and that probably some additional species is involved in the oxidation. The marked catalytic effect on the Guyard reaction by agents which complex and hence stabilize manganese(III) was reported by Polissar and by Tompkins.[6] This feature suggests that the manganese(II)-manganese(III) oxidation couple may be in equilibrium with the manganate(VI)-permanganate couple. Manganate(VI) is then assumed to be the active species effective in the initial oxidation of manganese(II). Manganate(VI), which is a very powerful oxidizing agent, would normally be present in very low concentration in the acid solutions. However its concentration would be increased by agents which complex manganese(III) so that it could then serve as an effective oxidant of manganese(II) Such equilibrium would be consistent with the rapid exchange between manganese(II) and manganese(III) observed by Polissar,[7] the rapid exchange between permanganate and manganate(VI)[8] and the very slow exchange between manganese(II) and permanganate.[9] A rapid equilibrium between some solution species of manganese(IV) and manganese(II) with manganese(III) has been offered as an explanation of manganese(II)-manganese(III) exchange but has not really been proved. Thus the rapidly established equilibria are postulated to be

$$\mathrm{Mn^{IV}} + \mathrm{Mn^{II}} \rightleftarrows 2\mathrm{Mn^{III}};\ K_1 = \frac{[\mathrm{Mn^{III}}]^2}{[\mathrm{Mn^{II}}][\mathrm{Mn^{IV}}]} \quad (5)$$

and

$$\mathrm{Mn^{II}} + \mathrm{MnO_4^-} \rightleftarrows \mathrm{Mn^{III}} + \mathrm{MnO_4^{=}};\ K_2 = \frac{[\mathrm{Mn^{VI}}][\mathrm{Mn^{III}}]}{[\mathrm{Mn^{II}}][\mathrm{MnO_4^-}]} \quad (7)$$

No attempt has been made to identify the complex species. K_2 as written would certainly increase with iodate concentration while the dependence of K_1 cannot be stated. The equilibrium constants which include concentration terms as indicated may, of course, be expected to be valid only under constant ionic atmosphere conditions which are essentially fixed by the perchloric acid concentrations. The actual oxidation then requires two steps.

$$\mathrm{Mn^{II}} + \mathrm{MnO_4^{=}} \longrightarrow 2\mathrm{Mn^{IV}};\ \text{rate} = R_1 \quad (8)$$

A result of the oxidation of manganese(II) in this step will be an increase in the manganese(III) in the solution by the action of equilibrium 5. An additional step would yield the final products

$$\mathrm{Mn^{III}} + 2\mathrm{IO_4^-} \longrightarrow \mathrm{MnO_4^-} + 2\mathrm{IO_3^-};\ \text{rate} = R_2 \quad (9)$$

This last step indicates the over-all result of reactions 3 and 4. The rate expressions for these two equations are taken as

$$R_1 = k_1[\mathrm{Mn^{II}}][\mathrm{Mn^{VI}}] \quad (10)$$

and

$$R_2 = k_2[\mathrm{Mn^{III}}][\mathrm{H_5IO_6}]^2 \quad (11)$$

Very likely, k_2 may include a dependence upon the iodate concentration.

If the concentration of manganate(VI) is very low, then

$$D[\mathrm{Mn^{VI}}] = 0 \quad (12)$$

and

$$-(D[\mathrm{Mn^{II}}] + D[\mathrm{Mn^{III}}] + D[\mathrm{Mn^{IV}}]) = D[\mathrm{MnO_4^-}] = R_2 - R_1 \quad (13)$$

The conservation of electrons in the lower three oxidation states of manganese requires

$$2D[\mathrm{Mn^{II}}] + 3D[\mathrm{Mn^{III}}] + 4D[\mathrm{Mn^{IV}}] = 6R_1 - 3R_2 \quad (14)$$

Since $D(K_1) = 0$, it follows that

$$\frac{D[\mathrm{Mn^{IV}}]}{[\mathrm{Mn^{IV}}]} + \frac{D[\mathrm{Mn^{II}}]}{[\mathrm{Mn^{II}}]} - \frac{2D[\mathrm{Mn^{III}}]}{[\mathrm{Mn^{III}}]} = 0 \quad (15)$$

These differential equations have not been solved for a general case. However, under certain limiting conditions expressions for the rate can be obtained for situations which may be expected to approximate closely the actual experiments. Equations 13–15 may be rearranged to give

$$D[\mathrm{Mn^{II}}] = -3R_1 + D[\mathrm{Mn^{IV}}] \quad (16)$$

$$D[\mathrm{Mn^{III}}] = 4R_1 - \mathrm{R}_2 - 2D[\mathrm{Mn^{IV}}] \quad (17)$$

$$D[\mathrm{Mn^{IV}}] = \frac{[\mathrm{Mn^{IV}}]\,\{3R_1[\mathrm{Mn^{III}}] + (8R_1 - 2R_2)[\mathrm{Mn^{II}}]\}}{([\mathrm{Mn^{II}}][\mathrm{Mn^{III}}] + [\mathrm{Mn^{III}}][\mathrm{Mn^{IV}}] + 4[\mathrm{Mn^{II}}][\mathrm{Mn^{IV}}])} \quad (18)$$

Now under the conditions in which the starting material is manganese(II) and only a limited amount of iodate is present, *e.g.*, 10^{-3} molar, one would expect during most of the reaction that $[\mathrm{Mn^{II}}] \gg [\mathrm{Mn^{III}}] \gg [\mathrm{Mn^{IV}}]$. Under such conditions it follows from the above equations that

$$4R_1 = R_2 \quad (19)$$

or

$$4k_1[\mathrm{Mn^{II}}][\mathrm{Mn^{VI}}] = k_2[\mathrm{Mn^{III}}][\mathrm{H_5IO_6}]^2 \quad (20)$$

When $[\mathrm{Mn^{VI}}]$ is replaced by its value from K_2, equation 7, an expression for $[\mathrm{Mn^{III}}]$ obtains

$$[\mathrm{Mn^{III}}] = 2\sqrt{k_1K_2/k_2}\,[\mathrm{MnO_4^-}]^{1/2}[\mathrm{Mn^{II}}]/[\mathrm{H_5IO_6}] \quad (21)$$

Using equations 11, 13 and 19 with this result yields

$$D[\mathrm{MnO_4^-}] = R_2 - R_1 = 3/4R_2 = 3/2\sqrt{k_2\ k_1K_2}\,[\mathrm{MnO_4^-}]^{1/2}[\mathrm{Mn^{II}}][\mathrm{H_5IO_6}] \quad (22)$$

This is the kinetics law, equation 6, found experimentally.

These equations can also be applied to the case in which $[\mathrm{Mn^{III}}] \gg [\mathrm{Mn}]^{\mathrm{II}} \gg [\mathrm{Mn^{IV}}]$. Under these conditions $R_2 = R_1$, and the kinetics expression becomes identical with the observed expression, equation 2. According to these ideas, if a large excess of complexing agent were used, a major fraction of the manganese would be stored as manganese(III) complex so that the kinetics should then become second order in periodic acid. A series of reactions were carried out in which the starting solution was a 0.5 molar iodic acid solution saturated with manganese(II) iodate. It was found in these cases that although there was a fairly extended induction period, the rate at the inflection point did approach a second order in the periodic acid concentration for the higher values.

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[6] (a) M. J. Polissar, *J. Phys. Chem.*, **39**, 1057 (1935); (b) F. C. Tompkins, *Trans. Faraday Soc.*, **38**, 131 (1942).

[7] M. J. Polissar, THIS JOURNAL, **58**, 1372 (1936).

[8] H. C. Hornig, G. L. Zimmerman and W. F. Libby, *ibid.*, **72**, 3808 (1950).

[9] A. W. Adamson, *J. Phys. Colloid Chem.*, **55**, 293 (1951).

The short induction period in the case of the manganese(III) oxidation could well be due to manganese(II) present as a result of the disproportionation equilibrium of the manganese(III). This manganese(II), until it was nearly depleted, would reduce permanganate as it was formed. It is interesting to note that according to this mechanism manganese(IV) is reduced to the reactive manganese(III) state by manganese(II). If the manganese(IV) should accumulate until its concentration was greater than manganese(II), then the excess would be trapped in that state. Experimentally it was apparent from the final optical densities, that very appreciable fractions of the manganese did not reach permanganate. The loss of permanganate usually occurred at the high rates under conditions that the proposed mechanism would predict a high manganese(IV) level. It sometimes approached concentrations of 10^{-4} molar. The presence of an additional species was indicated also by a higher absorption at shorter wave lengths, and the ratio O.D. (3600 Å.)/O.D. (5260 Å.) which was about 0.5 for pure potassium permanganate was increased to greater than 1.0 in some of the solutions. The solutions were stable to change of absorption characteristics for several hours after the runs. However, if they were heated, additional permanganate color would develop. They appeared to be unstable to precipitation; and after a period of about a day when stored, sometimes yielded a visible red-brown precipitate. This completeness of the reaction is one of the features requiring the use of a standard similar to the sample in quantitative analyses by the colorimetric procedure employing periodate as recommended by Willard and Greathouse.[10]

The role of hydrogen ion would be difficult to evaluate experimentally. It could logically be expected to influence a number of steps in the reaction by affecting the degree of ionization of iodic, periodic and manganic(VI) acid or the hydrolysis of the manganese(III) and -(IV) species.

Some of the thermodynamic features of the system can be calculated from estimates of the standard $E°$ values of half cells for manganese oxidation–reduction reactions. The following values were used: $E°(\mathrm{Mn^{II}}, \mathrm{Mn^{III}}) = -1.6$ v. estimated by Taube.[11] From Latimer[12] for acid solutions: $E°(\mathrm{Mn^{II}}, \mathrm{MnO_2}) = -1.28$ v., $E°(\mathrm{MnO_2}, \mathrm{MnO_4^{=}}) = -2.23$ v. and $E°(\mathrm{MnO_4^{=}}, \mathrm{MnO_4^-}) = -0.54$ v. In using these values the second ionization constant of manganic(VI) acid was estimated by Ricci's rule[13] to be 10^{-2}. In the strongly acid solutions therefore the predominant manganese(VI) species was assumed to be $\mathrm{HMnO_4^-}$, and the equilibrium constants were calculated for this species. Thus in the absence of complexing agents K_2, as written in equation 7, would be *ca.* 10^{-16} in a solution of unit hydrogen activity. In a solution with $[\mathrm{MnO_4^-}] = [\mathrm{Mn^{++}}] = 10^{-4}$ *M*, the equilibrium value of $[\mathrm{Mn^{III}}]$ and $[\mathrm{HMnO_4^-}]$ would therefore be 10^{-12} *M*. Such a low concentration should be unable to support a rapid oxidation of manganese(II) according to equation 8 in agreement with the slow initial oxidation of manganese(II) by permanganate in the absence of complexing agent. This value of $[\mathrm{HMnO_4^-}]$ is well in excess of the value for the disproportionation equilibrium of manganate(VI), *i.e.*

$$3\mathrm{HMnO_4^-} + \mathrm{H^+} \longrightarrow \mathrm{MnO_2} + 2\mathrm{MnO_4^-} + 2\mathrm{H_2O} \quad (23)$$

However, this reaction must compete kinetically with the oxidation of manganese(II) ion and if much slower would not influence the reaction significantly.

It was also computed that the equilibrium concentration, $[\mathrm{Mn^{+++}}]$, in equilibrium with 10^{-4} *M*. $\mathrm{Mn^{++}}$ and $\mathrm{MnO_2}$ is *ca.* 10^{-8} *M*. The effectiveness of iodate as a complexing agent is indicated by the fact that in 1 *M* $\mathrm{HIO_3}$, concentrations of manganese(III) of nearly 10^{-3} *M*, have been obtained for which the solubility is limited by a red-brown precipitate which contains an approximately equimolar ratio of manganese and iodine and hence cannot be $\mathrm{MnO_2}$. Accordingly, the concentration of manganese(III) and correspondingly of manganate(VI) can be expected to be increased by several orders of magnitude by the presence of iodate. This would increase the manganate(VI) concentration to values at which it could readily support the reaction through the path including reaction 8 as proposed.

Preliminary experiments in 1.0 *M* $\mathrm{HIO_3}$ have supported some of the features of this mechanism. Because of the complexing ability of iodate appreciable concentrations of manganese(III) and manganese(IV) can be attained and measured. This work indicates that it may be possible actually to evaluate the equilibrium constant, K_1, for reaction 5 and the constant for the equilibrium between the iodate–periodate couple and the manganese(IV)–permanganate couple.

$$3\mathrm{IO_4^-} + 2\mathrm{Mn^{IV}} \rightleftarrows 2\mathrm{MnO_4^-} + 3\mathrm{IO_3^-} \quad (24)$$

Adamson[8] has proposed that equilibrium 5 is established slowly in the absence of complexing agents; in the iodic acids solution it is approached very rapidly. On the other hand, equilibrium 24 was established slowly in these solutions. Strictland and Spicer[2] required a rapidly established equilibrium for their mechanism.

The mechanism described seems to offer a reasonable course for the oxidation steps and leads to limiting rate expressions which agree closely to the experimental values of the maximum rates. Equation 6 describes the kinetics only after sufficient permanganate has been formed to permit most of the oxidation to follow the steps listed. In particular, it does not describe the early portion of the reactions. This may be because the initial steps of the oxidation must be accomplished by other slow processes which become relatively less important as more permanganate forms. A correlation of the induction periods with the concentration variables might yield useful information about these initial reactions. However, a study of the early portions of the reaction must be complicated by the fact that at least two competing processes

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(10) H. H. Willard and L. H. Greathouse, THIS JOURNAL, **39**, 2366 (1917).

(11) H. Taube, *ibid.*, **70**, 3928 (1948).

(12) W. M. Latimer, "The Oxidation States of the Elements and their Potentials in Aqueous Solutions," Prentice–Hall, Inc., New York, N. Y., 1938, p. 225.

(13) J. E. Ricci. THIS JOURNAL, **70**, 109 (1948).

proceed simultaneously. A complete description of the reaction rate appears to be a formidable task. Certainly this complex and interesting system deserves further study.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

Solubilization of Dodecylammonium Thiosulfate in Dodecylammonium Bromide Solutions at 50°[1]

BY I. M. KOLTHOFF AND W. F. JOHNSON

A new type of solubilization is described which consists of the solubilization of an insoluble salt of a detergent in solutions of freely soluble salts of the detergent. A study of the solubility of slightly soluble dodecylammonium thiosulfate in solutions of dodecylammonium bromide showed that below the critical concentration the dodecylammonium bromide behaves as a normal strong univalent electrolyte in suppressing the solubility of the thiosulfate. Above the critical concentration the solubility of the thiosulfate salt was found to increase linearly with the concentration of the bromide salt. This solubilization is explained by an exchange between bromide and thiosulfate ions on the micelles, resulting in a decreased concentration of free thiosulfate ions in the solution. The solubility product of dodecylammonium thiosulfate was found to be 3.8×10^{-9} at 50°.

Solubilization of organic compounds in aqueous micellized solutions of detergents is considered to occur for apolar substances in the "sandwich" layer between the two parts of the micelle and for polar substances between the parallel paraffin chains.

A new type of solubilization is considered in this paper. Confining ourselves to a cationic detergent the solubilization described below is that of a slightly soluble salt of the detergent in a solution of a freely soluble salt of the detergent. According to the mass action law effect the solubility of a slightly soluble salt of a cation detergent decreases in a solution of a freely soluble salt of the cation detergent until the critical concentration of the latter is attained. When the concentration becomes greater than the critical concentration micelles are formed, anions being the counter ions of the micelle. These anions adsorbed on the micelle can exchange with other anions in the bulk of the solution. Denoting by DA the slightly soluble salt of the detergent and by DB the freely soluble salt we have above the critical concentration,

$$(\mathrm{Mic}^{n+})\Bigg|\; n\mathrm{B}^- + y\mathrm{A}^- \rightleftarrows (\mathrm{Mic}^{n+})\Bigg|\begin{array}{l}(n-x)\mathrm{B}^-\\ \text{and}\\ x\mathrm{A}^-\end{array} \begin{array}{l} \\ + x\mathrm{B}^- +\\ (y-x)\mathrm{A}^-\end{array}$$

By this exchange A^- ions are withdrawn from solution, and the apparent solubility will increase above the critical concentration. Dependent on the equilibrium in the above reaction the solubility of DA may become much greater in DB solution than in water.

What has been said for cationic detergents also holds for anionic detergents. It is to be expected that for the reason given above that a slightly soluble fatty acid soap will be solubilized by a freely soluble soap, which not necessarily has to be derived from the same fatty acid.

In the present study we have determined the solubility of the slightly soluble salt, dodecylammonium thiosulfate, in solutions of the free soluble cationic detergent, dodecylammonium bromide.

Dodecylammonium thiosulfate is only slightly soluble in water at 50°, but is soluble to a much greater extent in solutions of dodecylammonium bromide. This investigation of the solubilization of dodecylammonium thiosulfate was made primarily as a preliminary to a study of the reaction between thiosulfate ion and dodecyl bromide in solutions of dodecylammonium bromide.

Experimental

Dodecylammonium thiosulfate was prepared by adding dropwise a one molar solution of sodium thiosulfate and dodecylammonium chloride (in 50% ethanol–water solution) to approximately 1.5 liters of conductivity water maintained at about 70°. The solution was kept well stirred during the precipitation. As nearly as possible the dodecylammonium chloride solution was added at twice the rate at which the sodium thiosulfate solution was added to prevent an excess of either reagent accumulating during the precipitation. The solid dodecylammonium thiosulfate floated to the surface and was skimmed off with a watch glass. The product was transferred to a büchner filter funnel and washed several times with water, sucked dry and dried in a vacuum desiccator over anhydrous magnesium perchlorate at room temperature.

Dodecylammonium bromide was prepared by passing 99.2% pure tank hydrogen bromide into a benzene solution of dodecylamine. The dodecylamine used was a sample obtained from Armour and Company. The amine was fractionally distilled through a 20-inch column. The salt was recrystallized twice from benzene and twice from absolute ethanol and dried in a vacuum desiccator.

Analysis of the solutions was accomplished by titration with standard iodine solution, using the rotating platinum micro-electrode to detect the end-point amperometrically. In order to test the effect of micellized dodecylammonium bromide on the titration, the following experiments were carried out. To approximately 90 ml. of 0.1 *N* dodecylammonium bromide solution contained in a 100-ml. volumetric flask immersed in a 50.0 ± 0.1° thermostat, 10.00 ml. of 0.1002 *M* sodium thiosulfate solution was added. The flask was removed from the thermostat and shaken to dissolve the precipitate of dodecylammonium thiosulfate which had formed. The flask was returned to the thermostat and allowed to stand for 15 minutes before the solution was made to volume. The solution was again shaken prior to the removal of 10.00-ml. samples for titration. The ten-ml. sample was added to 20 ml. of absolute alcohol and titrated with 0.01000 *N* iodine solution. Similar experiments were carried out in which the concentrations of sodium thiosulfate and iodine were one-tenth of those given above.

For the titration of the 0.01002 *N* sodium thiosulfate solutions the average error and average deviation of a single determination from the mean were both 0.2%. With 0.001002 *M* sodium thiosulfate solution the average error of

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