of the results obtained in the present investigation for the system zinc–bismuth. Reference is here made to Fig. 6, which contains these results as well as the experimental points given by Spring and Romanoff and by Haas and Jellinek. It will be noticed that there is a very large difference between our results and those of the earlier workers. Thus we find here a critical temperature of about 605°, while the value accepted previously is between 750 and 800°.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, GEORGE WASHINGTON UNIVERSITY]

Evidence for Preferential One-Step Divalent Changes in the Molybdate-Catalyzed Reduction of Perchlorate by Stannous Ion in Sulfuric Acid Solution

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The study of kinetics of the molybdenum-catalyzed reduction of perchlorate ion by stannous ion in sulfuric acid solution follows the law given in equation (1). A reaction mechanism which fits this law is proposed and scrutinized. Evidence for direct bivalent reduction of molybdate is presented and its bearing on current controversy concerning one- and two-electron reductions is discussed. Other possible molybdenum-catalyzed reductions are mentioned.

Introduction

It is well known that the perchlorate ion, although potentially a strong oxidant is reduced only with difficulty under usual conditions. A recent polarographic study has disclosed the powerful catalytic activity of molybdate and pentavalent molybdenum toward reduction of perchlorate at a mercury electrode.[1] An extension of this work, the subject of this paper, has now demonstrated that molybdate maintains its catalytic activity in the reduction of perchlorate by stannous ion. Inquiry into mechanism gives strong indication that the catalytic species is tetravalent molybdenum, a valence state which is unstable in solution. Moreover our evidence leads to the interesting conclusion that hexavalent molybdenum (molybdate) is reduced to the tetravalent state by stannous ion through a process which bypasses the easily accessible valence of five.

This last observation directly contradicts the theory of compulsory univalent oxidation of Michaelis[2] and of Haber and Weiss.[3]

So many violations of this principle may be found, violations which are most frequently encountered in oxidation–reduction reactions of covalent compounds, that only a few representative illustrations may be given here. For example electrophilic displacement of hydrogen of one carbonium ion by another as in hydrogen–halogen exchange, the nucleophilic displacement on halogen of one carbanion by another, and the exchange of oxygen between sulfate and sulfite are quite apparently oxidation–reduction reactions. Nevertheless they are closely analogous to other displacement processes such as the solvolysis of alkyl halides which are not normally regarded as oxidations. Whereas such illustrations in no way rule out simple electron transfer as a possible route for an oxidation–reduction process it must be borne in mind that most inorganic ions, especially those which participate in such processes, possess covalently bound structures. We are of the opinion that the process involved in our study is an oxidation–reduction reaction of the displacement type.

Procedure.—Analytical grade reagents were employed in all experiments. Stannous solutions were standardized with potassium permanganate immediately before use. The reaction was carried out in 2.5 *M* sulfuric acid in a round-bottom flask suspended in a thermostat at 25°. The reaction was started by adding a few milliliters of molybdate solution to a solution of stannous ion (as chloride) and perchloric acid in sulfuric acid. No perceptible reaction took place in the absence of molybdate in agreement with a report from Dr. R. Rivest.[4] Air was removed from reagents and again at the start of the reaction by bubbling nitrogen through the solutions. Continuous bubbling through the course of the reaction proved unnecessary. At various intervals samples of the reacting mixture were removed and titrated with standard permanganate solution to determine the amount of stannous ion remaining. This titration also included the reduced molybdenum, but this was for the most part insignificant and was ignored.

Experimental Observations and Results.—The reaction mixture at the beginning turns dark blue and becomes pale yellow as the reaction proceeds when the molybdate concentration is as high as 10^{-3} *M*. When the molybdate concentration is lower by tenfold the initial color is yellow and the solution becomes colorless to the eye as the reaction proceeds. Spectrophotometric studies showed that the concentration of pentavalent molybdenum during the latter part of the reaction was less than half the total molybdenum concentration. The intense initial coloration made spectrophotometric studies of the change in pentavalent molybdenum impossible to interpret because of lack of knowledge of interference of other valences of molybdenum. Two such studies are reproduced in Fig. 1. Perchlorate ion is reduced to chloride ion and stannous tin is oxidized to stannic tin.

Analysis of a variety of runs with equivalent concentrations of Sn^{++} and ClO_4^- and excess quantities

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* Chemistry Department, University of Kansas, Lawrence, Kansas.

[1] G. P. Haight, Jr., *Anal. Chem.*, **23**, 1505 (1951).

[2] L. Michaelis, *Trans. Electrochem. Soc.*, **71**, 107 (1937); *Ann. Rev. Biochem.*, **7**, 1 (1938).

[3] Haber and Weiss, *Naturwissenschaften*, **20**, 948 (1932); *Proc. Roy. Soc. (London)*, **A142**, 332 (1934); *Nature*, **133**, 648 (1934); *Naturwissenschaften*, **23**, 64 (1935).

[4] *Private communication from Dr. R. Rivest, University of California.*

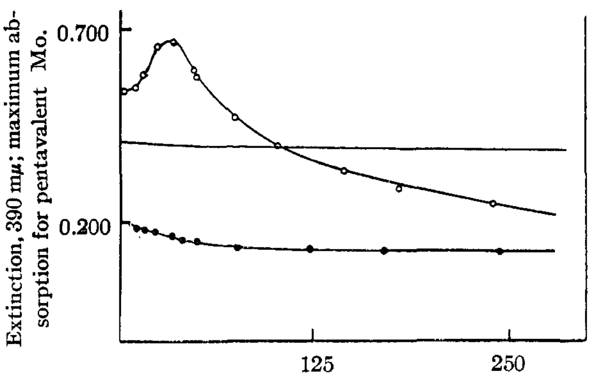

Fig. 1.—Change of spectrophotometric extinction at 390 mμ during run 3 in which Mo was added initially in the hexavalent state (solid dots) and in the pentavalent state (open dots). Horizontal line shows pentavalent Mo with no Sn^{++} or ClO_4^- present.

of each with various concentrations of $MoO_4^=$ leads to the expression

$$\frac{d(Sn^{++})}{dt} = \frac{K(Sn^{++})^{\frac{3}{2}}(ClO_4^-)^{\frac{3}{2}}(Mo^t)^{\frac{1}{2}}}{1 + 4K'(ClO_4^-)} \quad (1)$$

which on integration becomes

$$\frac{1 + \frac{A}{(Sn^{++})}}{\left(1 + \frac{2A}{(Sn^{++})}\right)^{\frac{1}{2}}} + AK'\left(1 + \frac{2A}{(Sn^{++})}\right)^{\frac{1}{2}} = \frac{A^2K}{8}(Mo^t)^{\frac{1}{2}}t + c \quad (2)$$

(Mo^t) refers to total Mo concentration in all valences; $A = \frac{1}{2}\left[4(ClO_4^-)_0 - (Sn^{++})_0\right]$, where $(ClO_4^-)_4$ and $(Sn^{++})_0$ are initial concentrations.

If A is 0 equation (2) becomes

$$\frac{1}{2(Sn^{++})^2} + \frac{K'}{(Sn^{++})} = \frac{K}{8}(Mo^t)^{\frac{1}{2}}t \quad (3)$$

The rate of the reaction is roughly proportional to the square of the hydrogen ion concentration which was measured for each run and corrections made where N H_2SO_4 deviated from 5. K' was evaluated from runs 1 and 9. Values of K calculated for each run are shown in Table I. These values are in fair agreement and show no definite trends except perhaps a small tendency to decrease with decreasing molybdenum concentration. This trend is explained in the discussion of a possible mechanism. The authors feel this agreement is very good considering the complexity of the system. Figure 2 shows plots of the left-hand portion of equation (2) *vs.* time for the best run. Most runs were nearly this good in yielding straight line plots. Changes in ionic strength were necessarily small due to the high concentration of sulfuric acid used, but one change of 6% in the sulfate ion concentration failed to alter the reaction rate. Addition of stannic chloride in amount equal to the original stannous ion concentration failed to alter the rate of the reaction indicating that neither stannic tin nor chloride ion influences the kinetics.

TABLE I

STARTING CONDITIONS AND CONSTANTS FOR VARIOUS RUNS

	$N_{Sn^{++}}$	$N_{ClO_4^-}$	$M_{(Mo^t)}$	$N_{H_2SO_4}$	K for Actual rate law $K' = 8.15$
1	0.2264	0.2756	2.7×10^{-3}	5.00	1010
2	.1988	.2000	1.35×10^{-3}	5.67	932
3	.1988	.2000	4.50×10^{-4}	5.64	1010
4	.2264	.2756	2.70×10^{-4}	5.00	1070
5	.2264	.2756	1.35×10^{-4}	5.00	773
6	.2264	.2756	6.75×10^{-5}	5.00	709
7	.2264	.5512	2.70×10^{-4}	5.00	1060
8	.2264	.5512	6.75×10^{-5}	5.00	924
9	.2264	2.756	1.35×10^{-4}	5.00	958
10	.1988	2.840	4.50×10^{-5}	5.67	748
11	.1868	0.1152	1.35×10^{-3}	5.02	692
12	.1868	0.1752	1.35×10^{-3}	5.55	876

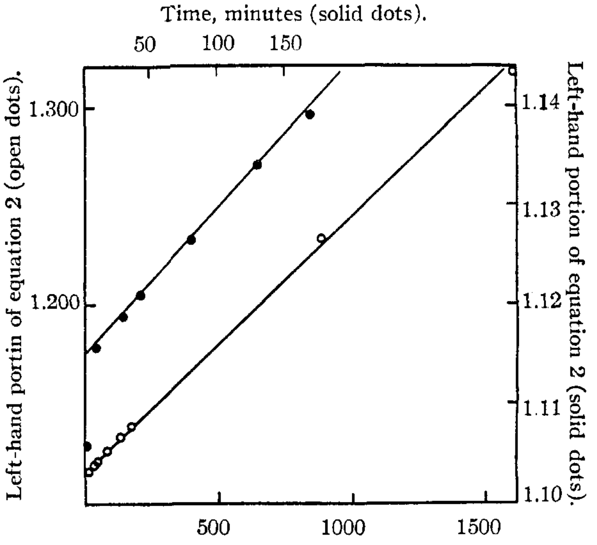

Fig. 2.—Best run, Run 5. Most lines were nearly this good. This shows the error to be expected in calculating K from slopes: upper line, first 2.5 hr.; lower line 25 hr. Note initial surge; A = 0.0123.

Reaction Mechanism.—The following possible mechanism is in agreement with the kinetics of the reaction and with various auxiliary evidences to be discussed. Because so little is known concerning the species of molybdenum in any of its valence states these valence states are indicated simply by the symbol "Mo" with superscripts denoting the valence states in question. Complexes are also postulated whose detailed structures cannot be elucidated and these will be indicated simply by "Mo" with a valence state superscript combined with complexing agent. For example Mo^6ClO_4 will indicate a complex between molybdate and perchlorate with no attempt made to guess at the amount of hydrogen, other oxygen or charge present in the species. The choice of rate constants $(k_3)^2$, $2k_3k_4$ and k_4^2 is explained in the discussion of the reaction mechanism.

A Possible Reaction Mechanism

$$Mo^6 + ClO_4^- \rightleftarrows Mo^6ClO_4 \qquad K_1$$

$$Mo^6ClO_4 + Sn^{++} \longrightarrow Mo^4 + ClO_4^- + Sn^{++++} \qquad k_1$$

$$Mo^4 + ClO_4^- \rightleftarrows Mo^4ClO_4 \qquad K_2$$

$$Mo^4ClO_4^- + Sn^{++} \longrightarrow Mo^4 + ClO_3^- + Sn^{++++} \qquad k_2$$
(slow step)

$$\mathrm{Mo^4 + Mo^4 \longrightarrow Mo^5 + Mo^3} \qquad (k_3)^2$$

$$\mathrm{Mo^4 + Mo^4ClO_4 \longrightarrow Mo^5 + Mo^3 + ClO_4^-} \qquad 2k_3k_4$$

$$\mathrm{Mo^4ClO_4 + Mo^4ClO_4 \longrightarrow Mo^5 + Mo^3 + 2ClO_4^-} \qquad (k_4)^2$$

$$\mathrm{Mo^3 + Oxidants \longrightarrow Mo^5\ (very\ fast)}$$

$$\mathrm{Mo^5 + Oxidants \longrightarrow Mo^6} \qquad k_5$$

$$\mathrm{Mo^4 + Oxidants \longrightarrow Mo^4\ Oxidants\ (complex)} \qquad k_6$$

$$\mathrm{Mo^4\ Oxidants + Sn^{++} \longrightarrow Mo^4 + Inert\ Products}$$
(very fast)

Oxidants may be ClO_3^-, ClO_2^-, ClO^-, Cl_2, Cl_2O, ClO or ClO_2. Assuming K_1 and K_2 to be very small and using steady state arguments for concentrations of Mo^6, Mo^5, Mo^4 and oxidants, this set of equations agrees with kinetic equation (1). In the steady state expressions which involve oxidants the assumption is made that the rate of oxidant formation equals the rate of the reduction of perchlorate. This will of course be true unless the process of reduction divides into several routes prior to appearance of the effective species. Derivation from the equations of the mechanism yields equation (1) with

$$K = k_2K_2(k_1K_1)^{\frac{1}{2}}/k_3\left(1 + \frac{K_1k_1k_6}{k_2k_2k_5}\right)^{\frac{1}{2}} \text{ and } K' = k_4K_2/k_3$$

Discussion of the Proposed Reaction Mechanism.—The high order of the reaction combined with the appearance of $^1/_2$ powers indicates a very complex system if the individual steps are to remain simple. Thus the large number of equations is not surprising. A mechanism involving rapid direct reduction of uncomplexed Mo^6 to Mo^4 by stannous ion without benefit of perchlorate catalysis also fits the kinetics if it is assumed that virtually all the molybdenum is pentavalent during the reaction. Colorimetric evidence (Fig. 1) shows this to be certainly not true. A semi-quantitative study of the direct reduction of Mo^6 to Mo^5 by stannous ion indicated that this reaction was too slow to yield steady state conditions at the speed achieved in the perchlorate reduction. It would thus appear that not only does molybdate catalyze the reduction of perchlorate, but perchlorate catalyzes the reduction of molybdate, a possible consequence of complex formation. Reduction to quadrivalent molybdenum is postulated as a result of indications that none of the three more stable valences is active. Hexavalent molybdenum is ruled out as a result of polarographic studies[1] which show that catalytic reduction of perchlorate begins only after reduction of molybdenum to the pentavalent form. Trivalent molybdenum is also ruled out on the basis of polarographic studies which indicate no catalytic reduction of perchlorate if molybdenum is present in the trivalent state alone. The results shown in Fig. 3 rule out pentavalent molybdenum as the active catalyst. When hexavalent molybdenum is used to start the reaction there is a large initial surge indicating very rapid reduction of ClO_4^- before steady state conditions are reached. When pentavalent molybdenum was used to start the reaction the approach to steady state was through an induction period of little or no reaction. This indicates to us that pentavalent molybdenum must be ruled out as the catalyst. Only tetravalent molybdenum is left. The fact that it disproportionates rapidly would help explain the $^1/_2$ powers in the formula for the kinetics. Direct reduction of hexavalent to tetravalent molybdenum would explain the initial surge in cases where molybdate was used to start the reaction and the parallel nature of the slopes in Fig. 3 indicates that it makes little difference what the initial valence state of molybdenum is once steady state conditions are achieved. The spectrophotometric plot in Fig. 1 is for the same runs shown in Fig. 3 showing that there is little correlation between the color changes and the kinetics. The catalysis by tetravalent molybdenum and the evident by-passing of the pentavalent stage leads to the speculation that the mechanism may involve oxygen atom transfer from molybdenum to stannous ion and from oxychloro ions to reduced molybdenum complexed therewith. This would account for one-step divalent changes in simple fashion. The requirement of low equilibrium constants for complexes fits the known lack of ability of perchlorate ion to form complexes yet does not eliminate the means of close approach of Mo^6 or Mo^4 necessary for catalytic activity. No scheme involving direct reduction of perchlorate by tetravalent molybdenum fits the reaction kinetics.

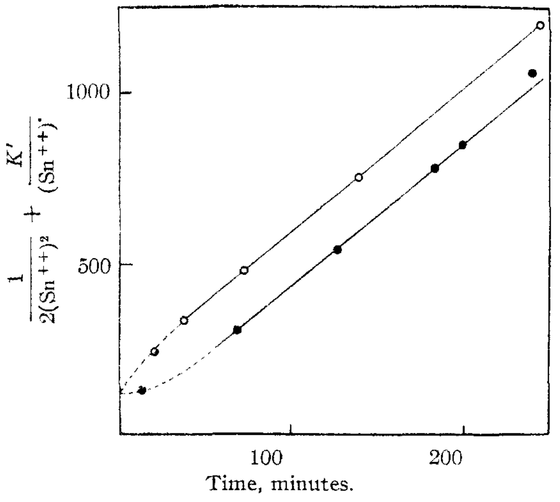

Fig. 3.—Run 2. Solid dots, Mo added in pentavalent state; open dots, Mo added in hexavalent state, showing induction period for pentavalent Mo; $A = 0$.

The appearance of $^1/_2$ powers in the kinetic expression suggests that Mo^4 is removed by a disproportionation reaction. Disproportionation of the perchlorate complex of Mo^4 was introduced to account for the term, $1 + 4K'(ClO_4^-)$, in the rate expression. The assumption of a binomial for the rate constants for the three disproportionations was made partly to achieve an expression which could be integrated. Disproportionation solely *via* uncomplexed tetravalent molybdenum leads to a rate law involving only the numerator of equation (1). Disproportionation *via* complexed tetravalent molybdenum requires square root dependence on perchlorate. Since both processes are indicated by the kinetics it is reasonable that the cross disproportionation should also participate. Assignment of a rate constant for this step which is the geometric mean weighted with a statistical factor of two is made in order to secure an integrable function. In all honesty it should be stated that the factor of two is based more on the requirements of integration than statistics. In any event the function is not very sensitive to the assignment of this constant, especially in the region of high perchlorate concentration. Also much of the variation in *K* is attributed to the error probably introduced here. It is also not only quite possible but likely that Mo^4 is removed in part by other reactions such as reaction with Mo^6 or with any of the many oxidants forming in the solution. This probably accounts for the apparent tendency of *K* to decrease slightly with decreasing molybdenum concentration.

Mo^3, if formed, must be rapidly oxidized for it is known that reduction of molybdate with stannous ion yields only pentavalent molybdenum.

If Mo^5 is produced, and is inert catalytically, it must be reoxidized to Mo^6, else the reaction would cease. Evidence that this probably occurs stems from the fact (unpublished) that the reduction of molybdate in perchloric acid by a Jones reductor yields only partial reduction to the pentavalent form, whereas in sulfuric or hydrochloric acid reduction proceeds smoothly to the trivalent state.

The removal of oxidants by complex formation followed by very fast reduction by stannous ion is postulated on the basis that it fits the reaction kinetics. Two experimental facts substantiate this assumption. The assumption predicts that at low stannous ion concentration equilibrium would be established between Mo^4 and oxidants, with a resultant build up of oxidant concentration and a speed up of the reaction as shown by the last two points on Fig. 4. In addition the reduction of chlorate ion by stannous ion in strong sulfuric acid is rather slow, but in the presence of molybdate, the reduction of chlorate to chloride by stannous ion is virtually instantaneous. This would indicate that although stannous tin probably reacts with the oxidants alone, it reacts very much faster in the presence of molybdenum.

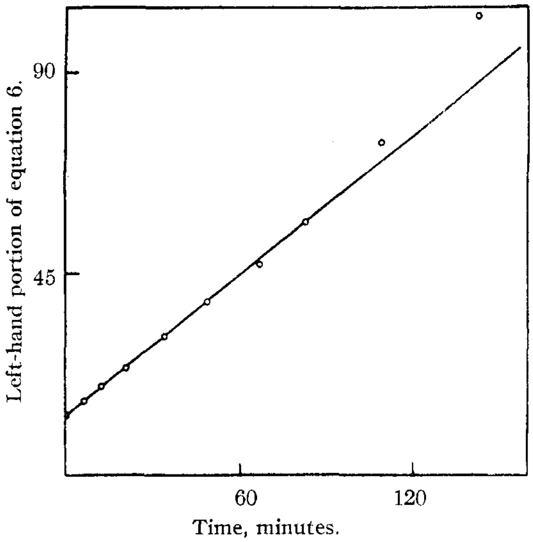

Fig. 4.—Run 9 showing deviation in favor of higher rate at very low (Sn^{++}); $A = 1.265$.

Besides elucidating the mechanism of a very complicated reaction, indicating a preference for one-step divalent reductions by stannous ion, and showing the catalytic activity of tetravalent molybdenum, this study indicates a promising new reducing agent may now be available. This Laboratory is now studying the reduction of nitrate, and nitro organic compounds with promising preliminary results. Its use for analysis of chlorates, perchlorates, nitrates and possible other oxy ions and compounds which may be irreversibly reduced is being investigated as well.

[CONTRIBUTION FROM THE GRASSELLI CHEMICALS DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND COMPANY, INC.]

Potassium Metaphosphate: Molecular Weight, Viscosity Behavior and Rate of Hydrolysis of Non-cross-linked Polymer

BY R. PFANSTIEL AND R. K. ILER

RECEIVED APRIL 18, 1952

New data are presented on the molecular weight, viscosity and rate of hydrolysis of a linear polymetaphosphate in an aqueous solution obtained by solubilizing crystalline KPO_3 by partial cation exchange with the sodium salt of an ion-exchange resin. The marked effect of minute variations in the original $K_2O:P_2O_5$ ratio on the viscosity indicates that when there is a deficiency of potassium in a KPO_3 melt, cross-linking occurs between the metaphosphate polymer chains in the resulting KPO_3 crystal. Excess potassium in a melt of KPO_3 does not reduce the molecular weight of KPO_3 by acting as a chain-stopper, but instead forms potassium tripolyphosphate as a separate phase. The accompanying KPO_3 is essentially non-cross-linked. The molecular weight of non-cross-linked KPO_3, determined in aqueous solution, may be as high as 120,000. The energy of activation of the hydrolysis of polymetaphosphate at *p*H 8.5 is about 25 kcal. per mole.

Introduction

Potassium metaphosphate, empirical formula KPO_3, crystallizes readily at 807° from a very fluid melt of the same composition. It gives no indication from this behavior that it is a linear inorganic polymer. Nevertheless, it has been known for many years that when this salt is brought into aqueous solution a highly viscous dispersion is obtained which is characteristic of a linear polymer of high molecular weight. It is the purpose of this paper to present new data on the molecular weight and on the viscosity and stability of aqueous solutions of KPO_3, and to demonstrate the marked effect of minute variations in the $K_2O:P_2O_5$ ratio on the viscosity of this salt in aqueous solution. The results suggest that cross-linking of the metaphosphate chains occurs as the ratio of $K_2O:P_2O_5$ in the KPO_3 crystal falls below unity.