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On the Hydrolysis of the Manganese(III) Ion

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The protolysis equilibria of the Mn^{3+} ion have been studied at 25 °C and in the ionic medium 3 M ($H^+ - Li^+$), ClO_4^- by measuring with iridium electrodes the redox potential of the $Mn^{3+} - Mn^{2+}$ couple as a function of the ratio $[Mn(III)][Mn^{2+}]^{-1}$ at acidity levels ranging from 0.26 to 3 M. The emf data may be explained by the equilibria

$Mn^{3+} + H_2O \rightleftharpoons MnOH^{2+} + H^+$;
$\log {}^*K_1 = 0.4 \pm 0.1$

and

$Mn^{3+} + 2H_2O \rightleftharpoons Mn(OH)_2{}^+ + 2H^+$;
$\log {}^*\beta_2 = 0.1 \pm 0.1$

The standard potential of the $Mn^{3+} - Mn^{2+}$ half-cell in 3 M lithium perchlorate medium has been determined to 1559 ± 3 mV.

For the study of equilibria in solutions possessing a slight redox buffer capacity an experimental approach is presented that may find a wide application.

The present communication represents the first part of a series dealing with the redox and the complex formation equilibria of the manganese(III) ion. A prerequisite for the correct interpretation of these reactions is that all the steps of the hydrolysis mechanism are ascertained, hence the choice of our first subject.

Since the Mn^{3+} ion represents a strong and rapid oxidizing agent, and it plays a central role in the complicated redox reactions involving permanganate and mangan dioxide, the hydrolysis and complex formation equilibria of the manganese(III) species have received considerable attention in the last decades.

In connection with a comprehensive kinetic study, Diebler and Sutin[1] have estimated, on the basis of the influence of the acidity level on the visible spectrum of manganese(III) perchlorate solutions, $\log {}^*K_1$ for the first step of hydrolysis to amount to such a high value as 0.3. Essentially the same conclusion was deduced by Fackler and Chawla[2] who have studied the spectra of the numerous manganese(III) complexes. Rosseinsky,[3] who first explored the conditions required to prepare stable manganese(III) perchlorate solutions, confirmed in a kinetic study, carried out in collaboration with Nicol, that the Mn^{3+} ion is an acid of exceptional strength and has given kinetic evidence for a $\log {}^*K_1$ value near to zero at 20 °C. A careful spectrophotometric investigation on this subject was published in 1967 by Wells and Davies[4] who concluded that the hydrolysis may be described by the formation of $MnOH^{2+}$ and have found $\log {}^*K_1 = \log [MnOH^{2+}][H^+][Mn^{3+}]^{-1}$ to equal 0.0 in 4 M perchlorate medium.

As in order to deduce this equilibrium constant the molar absorptivities of the reacting manganese species must be evaluated, it is understandable that the simplest hypothesis was chosen to describe the hydrolysis process.

In this work an attempt has been made to utilize the greater power of potentiometry for obtaining a detailed picture of the hydrolysis reaction. Our starting point was the pioneering investigation of Ciavatta and Grimaldi.[5] These authors have demonstrated that under the proper experimental conditions the $Mn^{3+} - Mn^{2+}$ couple yields reversible potentials, and they have given convincing evidence that the manganese(III) species prevailing in perchloric acid solutions are mononuclear.

METHOD OF INVESTIGATION

In the present work the hydrolysis equilibria have been studied by determining the formal standard potential of the Mn(III) – Mn^{2+} couple as a function of the hydrogen ion concentration.

In each experiment we started with a solution of the general composition Mn^{2+} B_0, H^+ H, Li^+ (3.00 M – 2 $B_0 - H$), ClO_4^- 3.00 M, which for the sake of compactness in the following discussion will be denoted by TS_0, while the solution arising from TS_0 by oxidation of the Mn^{2+} to Mn(III) will be symbolized by TS. Usually a B_0 value of around 15 mM has been chosen and in the different series of experiments the hydrogen ion concentration level, H, was made to increase from 0.26 to 3 M.

In an attempt to minimize the activity factor variation of the reacting species in TS, the perchlorate ion concentration was maintained at the 3 M level by introducing lithium perchlorate. This solvent salt was chosen since, according to the measurements of Rush and Johnson,[6] the activity factor of perchloric acid varies only slightly when at the ionic strength 3 M lithium ions are replaced by hydrogen ions. As the reference state 3 M $LiClO_4$ will be taken, thus the activity factors of the reacting species are defined to tend to unity as the composition of TS approaches this pure solvent salt solution.

In order to generate manganese(III) ions, the test solution was placed in the anode compartment of the electrolysis circuit

Au|TS|$HClO_4$ H, $LiClO_4$ (3.00 M – H)|
|$HClO_4$ 3.00 M, $AgClO_4$ 0.100 M|Ag
constant current supply

and ensuing each step of oxidation, involving usually the removal of a few tenths of a micromol of electrons from TS, the emf of the cell (R), where TS

$$\mathrm{RE}\,\Big|\,\mathrm{TS}\,\Big|\begin{array}{l}\mathrm{Au}\\ \mathrm{and}\ +\\ \mathrm{Ir}\end{array} \qquad \mathrm{(R)}$$

is the symbol for a solution of the composition Mn(III) B_3, Mn^{2+} ($B_0 - B_3$), $H^+ H$, Li^+ (3.00 M – $2B_0 - H$), ClO_4 3.00 M and

RE = |$HClO_4$ H, $LiClO_4$ (3.00 M – H)|$HClO_4$ 3.00 M, $AgClO_4$ 0.010 M|Ag

was determined.

The emf of this cell may at 25 °C be expressed by eqn. (1), where e_0 represents the standard potential,

$$E_R = e_0 + 59.16 \log \frac{[Mn^{3+}]}{[Mn^{2+}]} + e_j - e_{RE} \qquad (1)$$

e_j is the liquid junction potential arising between TS and the bridge solution, while the potential of the reference half-cell, RE, is denoted by e_{RE}. In some cases to save time a 3 M $LiClO_4$ solution was employed in the salt bridges, but of course some gain in accuracy was attained by choosing the same acidity level as in TS.

Because of the instability of the manganese(III) species, in the course of a series of oxidation experiments the maximum manganese(III) concentration we have been able to generate never exceeded 0.25 mM. As a consequence, either low yield at the anodic oxidation or inadvertent or intentional reconversion of Mn(III) to Mn^{2+} may influence appreciably the hydrogen ion concentration in TS_0 which was chosen to range between 0.3 and 3 M. We shall therefore introduce in the following calculations the approximation that the equilibrium concentration of hydrogen ions equals the starting value H.

The interpretation of the $E_R([\mathrm{Mn(III)}])_H$ data is further simplified by the fact that the hydrolysis of the manganese(II) ion is suppressed entirely[6a] in the acidity interval studied by us, and therefore the $[Mn^{2+}]$ value may always be set equal to $B_0 - [\mathrm{Mn(III)}]$.

For reasons that will be discussed in the second part of this section, we have generally not been able to attain a theoretical yield for the anodic oxidation of Mn^{2+} to Mn(III). In order to find the [Mn(III)] present in the test solution when E_R is being determined, we have been forced to withdraw a sample from TS and analyze it for [Mn(III)]. By the coulometric method of I_3^- analysis which is described in the Experimental Section, a few tenths of a micromol of Mn(III) could be determined with an uncertainty of 1 – 2 %. Thus the complication arising from the low current yield which at the lowest hydrogen ion concentration, 0.26 M, was as low as 36 %, did not significantly influence the accuracy of the $E_R([\mathrm{Mn(III)}])_H$ data.

After having terminated the electrolysis experiment, a slightly platinized platinum foil was inserted into TS and N_2 was replaced by H_2. In the presence of this catalyst the reaction

$$2Mn^{3+} + H_2 \rightarrow 2Mn^{2+} + 2H^+$$

has been found, by measuring E_R, to go to completion within a couple of hours.

When the E_R value indicated a practically complete reduction, the platinum foil was connected to the potentiometric equipment and we started with the determination of the emf of the cell (H), where

$$H_2|TS_0|RE+ \qquad (H)$$

we may use the symbol TS_0 as the hydrogen ion concentration change ensuing an oxidation reduction cycle is certainly less than the analytical uncertainty.

It took usually another 2–3 h to saturate TS_0 with hydrogen of the prevailing partial pressure and to obtain an emf value remaining constant to within 10 μV overnight.

The emf of cell (H) may at 25 °C be described by eqn. (2), where $p_{H_2} = p_{atm} - p_{H_2O}$. The relevant water

$$E_H = e_{RE} - 59.16 \log (H/\sqrt{p_{H_2}}) - e_j \qquad (2)$$

vapor pressure values could be estimated by interpolating Rush's and Johnson's osmotic coefficient data.[6]

By adding eqn. (2) to (1) and by substracting from the resulting equation the experimentally determined expression 59.16 log $\{[Mn(III)]p_{H_2}^{\frac{1}{2}}/[Mn^{2+}]H\}$ we may calculate for each point the value of the function (3) which does not contain the

$$e_0 + 59.16 \log \frac{[Mn^{3+}]}{[Mn(III)]} \equiv \varepsilon^0 \qquad (3)$$

terms e_j and e_{RE} complicating the evaluation of the $[Mn^{3+}]$ from the emf data.

This ε^0 function will serve as the basis for ascertainment of the hydrolysis mechanism. Before turning to this question which forms the subject of the Results Section, some *general comments on the experimental conditions* might be of value partly for enabling the reader to assess the accuracy of the final conclusions, and partly because the experience gathered in the course of this work seems to be utilizable for the study of other unstable oxidizing agents such as Ag^{2+} and Co^{3+}.

To prepare manganese(III) solutions of a concentration sufficient to obtain reversible redox potentials, one must primarily retard the establishment of the equilibrium

$$2Mn^{3+} + 2H_2O \rightleftharpoons MnO_2 + 4H^+ + Mn^{2+} \qquad (4)$$

which according to our preliminary data has a log K value in the vicinity of 8.4, and one must work with solutions containing a minimum amount of reducing contaminants.

These requirements exclude the introduction of reagent solutions (which inevitably contain contaminants and floating solid material catalyzing the attainment of equilibrium (4)) and necessitate *anodic oxidation*. We have not been able to prepare by ozonization MnO_2 or MnO_4^--free mangan(III) solutions.

In accordance with the experience of Ciavatta and Grimaldi[5] we have found a gold-plated platinum net as the most suitable anode material. Whatever precautions are taken to minimize by stirring the accumulation of Mn(III) in the vicinity of the anode and thereby the acceleration of equilibration (4), the decisive factor in building up a local excess of Mn(III) remains the current density. For obvious practical reasons this cannot be lowered under a certain level and a compromise is inevitable. We have applied current densities varying between 2 to 100 $\mu A/cm^2$ which enabled us to attain even at the lowest acidity level an [Mn(III)] value of 60 μM without the formation of visible amounts of MnO_2 on the anode surface.

With conventionally purified reagents one cannot attain a practical current yield, especially at low acidity, a great part of the generated Mn^{3+} is lost by route (4) ,and another is reconverted by the impurities to Mn^{2+}. We have attempted to solve this problem by a *preoxidation* procedure. Each series of E_R measurement was preceded by the generation of 50 to 100 μmol of manganese(III). A high portion of this amount always decayed (as it could be recognized by E_R measurement) oxidizing the contaminants in the ionic medium and the perchloric acid. This test solution was allowed to stand overnight, the anode was then replaced by a platinized platinum electrode and all the remaining manganese(III) was reduced by H_2. The anode was now reinserted, the H_2 replaced by N_2 and finally the principal series of measurements could be started. The efficiency of this *preoxidation* treatment was tested by several experiments.

First, we have found that a second purification step does not significantly improve the current yield for Mn^{3+} generation. More importantly, the theoretical current efficiency to within 1 % was attained both in a 3 M $HClO_4$ solution prepared from doubly recrystallized $HClO_4(H_2O)_2(s)$ and in a 3 M solution of this acid purified by preoxidation.

A further important point was to find an electrode material yielding reversible and stable *redox potentials* at manganese(III) concentrations as low as 10–20 μM. Iridium metal has proved to be superior to gold while, as it has been pointed out in Ref. 5, platinum has shown an erratic behavior and seemed to catalyze the formation of MnO_2. We must emphasize that at [Mn(III)] values exceeding 50 μM gold and iridium gave E_R data agreeing to within 1 mV and this result we consider as a test that our E_R measurements provide the correct redox potential of TS. Whenever the two metals differed, the iridium potential was higher and it was accepted as the true E_R value.

Another minor difficulty was encountered by the slow decline of E_R due to the *oxidation of water*

$$2Mn^{3+} + H_2O \rightarrow 2Mn^{2+} + 2H^+ + \tfrac{1}{2}O_2 \qquad (5)$$

In each series of experiments the last point, usually corresponding to the highest manganese(III) concentration, was measured for several hours to get an idea of the magnitude of this source of error. Independently of the acidity and the manganese concentration level, E_R was found to decrease with a rate of 0.02 to 0.01 mV per hour, thus for a complete series of measurements, requiring about 40 to 50 h, an error of about 1 mV arises by decomposition through route (5). This instability is of importance for us only at the 3 M $HClO_4$ level at which the [Mn(III)] was calculated to save time on the basis of coulometry. The E_R data were in these cases corrected for reaction (5); the magnitude of the correction has barely exceeded the experimental uncertainty.

Further details of our experimental approach are summarized in the following section.

EXPERIMENTAL

Manganese(II) perchlorate solutions have been prepared by oxidizing at room temperature manganese metal, being introduced in excess, by thallium(I) ions:

$$2\,Tl^+ + Mn(s) \rightarrow 2\,Tl(s) + Mn^{2+} \qquad (6)$$

At a log H value of around -3 this reaction proceeds rapidly while the rate of dissolution of manganese metal is negligible, consequently the hydrogen ion concentration of the thallium perchlorate reagent solution remains unchanged and no appreciable amounts of chloride ions are formed.

To prepare 0.5 l of 0.1 M manganese perchlorate solution by this method requires about 24 h. The completion of the oxidation was checked by withdrawing samples and testing them for the presence of Tl^+ by adding I^-. We were always working with so great volumes that no appreciable loss occurred by this sampling.

The manganese concentration of the resulting stock solution has been checked each time and it has always proved to agree with the value calculated on the basis of the amount of thallium perchlorate introduced to within 0.2 %. The manganese analyses were made gravimetrically by precipitating $MnNH_4PO_4H_2O$ as recommended by Winkler.[7]

Since the hydrolysis of the Mn^{2+} ion is negligible for log $H > -6$, the stoichiometric proton excess of the stock could easily be determined by titration with coulometrically generated hydroxide ions. The equivalence point was evaluated potentiometrically by using a glass electrode.

We encountered in this synthesis only one *difficulty*. All the high purity (designation 4 N) manganese samples commercially available have been found to contain a trace of MnS, originating presumably from the concentrated manganese sulfate solution which served as the catholyte when the metal was prepared. Contacting this impure metal with the $TlClO_4$ solution gave rise to the evolution of some H_2S which was driven out by the vigorous stream of N_2 that was allowed to pass through the perchlorate solution throughout the synthesis.

Our choice of *$TlClO_4$ as a reagent* was dictated by the narrow hydrogen ion concentration range available for the oxidation of manganese metal. At acidities exceeding 1 mM some chloride formation from ClO_4^- is inevitably occurring even at 0 °C, while at higher pH values $Mn(OH)_2$ may precipitate because of low buffer capacity.

Moreover, thallium perchlorate can conveniently be prepared in a state of high purity by oxidizing cathodically deposited thallium metal with oxygen [eqn. (7)] in a perchloric acid solution. Crystals may

$$O_2 + 4Tl(s) + 2H_2O \rightarrow 4Tl^+ + 4OH^- \qquad (7)$$

finally be obtained by adding an excess of $HClO_4$ and cooling.

This somewhat lengthy method must be used instead of dissolving commercial Tl_2CO_3 in perchloric acid. All the Tl_2CO_3 samples we could acquire were contaminated with chloride which could not be removed by recrystallization because the influence of temperature on the solubility of TlCl and Tl_2CO_3 is very similar. This complication might be of interest for the analytical chemists who often employ thallium carbonate as an ultimate standard. The only safe way to prepare this

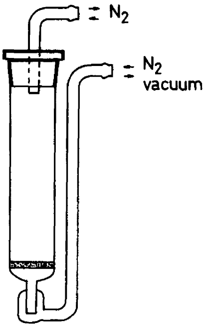

Fig. 1. Apparatus for the preparation of perchloric acid dihydrate.

substance in a state of high purity seems to be to introduce a stream of CO_2 in a solution of TlOH made by reaction (7) using a platinum vessel.

In the initial phase of this work *perchloric acid* solutions were made from crystalline perchloric acid dihydrate. This phase was separated from commercial perchloric acid of azeotropic composition at about −32 °C. Provided the viscous liquid was seeded with $HClO_4(H_2O)_2$, crystal formation was rapid and a yield of 10–20 % could be obtained. By two steps of crystallization the iron(III) and chloride contamination could be brought down to 0.1 μmol/mol $HClO_4$. The simple vessel shown in Fig. 1 was useful to agitate the solution, to protect it against atmospheric humidity and to remove the supernatant.

As we have discussed in the Method of Investigation section, the main part of the measurements was carried out with solutions of commercial perchloric acid purified by the preoxidation treatment. We consider the satisfactory agreement between the redox potential data with these two methods as an important argument for the reliability of our results.

The perchloric acid stock solutions were standardized either coulometrically or by titration against a sodium-free $KHCO_3$ preparation which serves as a primary standard in this laboratory; the analyses by the two approaches were found to agree to within 0.1 %.

Silver- and lithium perchlorate solutions were prepared and analyzed as usual in this laboratory.

In each series of redox potential measurements the test solution was protected by *a nitrogen stream;* floating matter was first removed by passing the gas through a tower filled with molecular sieve. The gas was then presaturated with water vapor and finally led through a sintered glass disc of porosity G4.

Gold electrodes were prepared by dipping a platinum gauze into a 0.1 M $AuCl_4^-$ solution containing hydrochloric acid. The gauze covered with a film of the gold solution was then inserted into an oven kept at 300 °C. At this temperature rapid decomposition to gold metal and chlorine occurs, and, provided the platinum support is clean, a coherent layer of gold is formed.

Any time we suspected the electrode was contaminated, the surface could be renewed by this treatment. In our experiments of one to two days duration, renewal often was necessary and usually entailed a redox potential increase of several mV's.

Gold deposited cathodically from a tetracyanoaurate solution has been found quite unsuitable as a redox electrode. Gold-plated platinum foils have always shown very low redox potential values and they could not be used either for the generation of Mn^{3+} ions. The failure is probably due to our inability to remove from the electrode surface the last traces of cyanide ions, they are known to form strong complexes with manganese(III).

When two gold electrodes were immersed in the same test solution, they agreed to within one or two mV's provided the [Mn(III)] exceeded 50–60 μM. This has also been found to be the case when one of the gold electrodes served as the anode. At lower manganese(III) concentrations, however, the gold electrodes have proved to be unreliable. In contrast to what we found at higher concentrations, several hours were needed to obtain a stationary redox potential value and electrodes prepared as identically as possible differed considerably. When one of the gold electrodes was employed as the anode, the difference often was as high as 5 mV.

These observations led us to believe that a thin layer of a gold oxide is formed on the electrode surface by oxidation with Mn^{3+}. Until the layer covers the surface, the manganese(III) concentration in the vicinity of the electrode will, because of the reaction, be lower than in the bulk. A further argument for this hypothesis is the observation that pretreatment with a manganese(III) solution entailed in many cases a considerable improvement. On the other hand in this case the electrode transfer, the necessary washing and the final drying often caused contamination, resulting in an unpredictable behavior. Moreover, we lose in this way the possibility to renew the active surface which represents a desideratum when working with solutions of a low redox buffer capacity.

No difficulties were encountered, however, by using *iridium* redox electrodes. At manganese(III) concentration levels as low as 10–20 μM they attained within a few minutes a constant redox potential value exceeding the gold electrode potential by several mV's. Moreover, when several iridium electrodes were inserted into the same test solution they never differed more than 1 mV. A

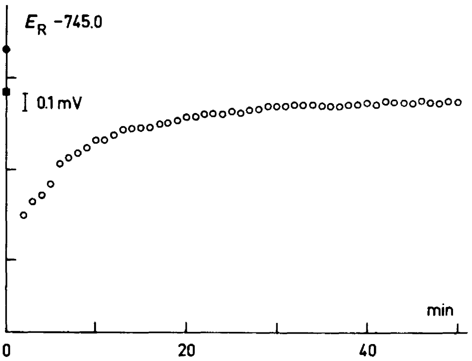

Fig. 2. Illustration of the behavior of the iridium electrodes. In a solution of $H = 1$ M, $[\mathrm{Mn(III)}] = 51$ μM and $[\mathrm{Mn}^{2+}] = 7.5$ mM two iridium electrodes were inserted. One of them was removed at zero time, was ignited and then reintroduced. ○, the reattainment of the reversible redox potential; ●, emf value prior to removal; ■, emf value of the second Ir-electrode.

typical experiment illustrating their excellent performance is shown in Fig. 2. Indeed, without the iridium electrodes we would not have been able to bring this investigation to a completion.

Unfortunately, we could not find a method for preparing a fresh iridium surface for each experiment. In an attempt to remove the impurities accumulated during the previous run, prior to a new series of measurements the iridium foils were brought, with a hydrogen-oxygen flame, to a temperature of around 2000 °C. Repetition of this ignition did not further improve the electrode behavior. In many cases, especially at the higher acidity levels, the ignition step could be omitted without influencing the results.

In view of this discussion it is easily understandable that whenever a difference of significance arose between the iridium and the gold electrodes, we always preferred the redox potential value shown by the former.

At the very low redox buffer capacity levels we had to work at, it was imperative to minimize the risk of contamination with reducing agents such as stopcock grease and the organic matter always present in the laboratory air. The vessel, illustrated in Fig. 3, which forms a part of a complete coulometric cell arrangement that has been described elsewhere, has proved therefore to be indispensable. Only the stopcocks containing the channels leading to the reference half-cell and the cathode compartments were coated lightly with silicon grease pretreated with 3 M $HClO_4$ and then washed with water and dried.

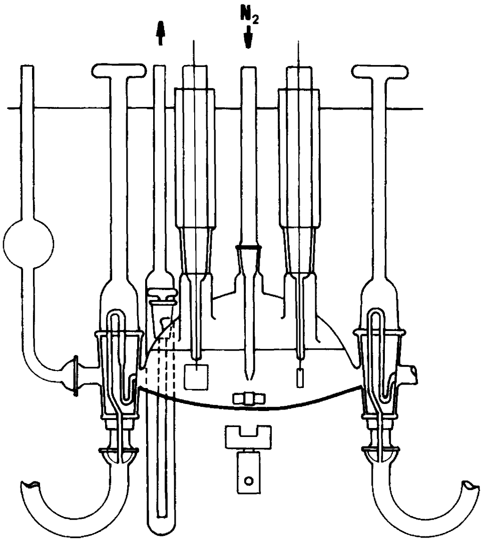

Fig. 3. All-glass vessel used for the redox potential measurements and for the generation of manganese(III) ions.

For the determination of the actual *manganese(III) concentration* 5.00 or 10.00 ml samples were withdrawn from the test solution and they were immediately introduced into a deoxygenated 0.1 M NaI solution. The reaction

$$2\mathrm{Mn}^{3+} + 3\mathrm{I}^- \rightarrow 2\mathrm{Mn}^{2+} + \mathrm{I}_3^- \qquad (8)$$

has been found to proceed to completion instantaneously even at the lowest manganese(III) concentration level studied in this work, 10 μM.

The amount of triiodide ions formed was determined potentiometrically, using Pt-foil electrodes, with coulometrically generated I_3^- ions. In each step about 0.15 μmoles of I_3^- were generated. Ensuing the anodic oxidation the redox potential, $E_{I_3^-}$, of the resulting solution was determined with at least two Pt-electrodes, one of them serving as the anode. Under the present conditions $E_{I_3^-}$, the emf of the redox half-cell against the silver reference half-cell, may simply be expressed by eqn. (9).

$$E_{I_3^-} = \eta^\circ - 29.58 \log \frac{\mu^\circ + \mu}{2} \qquad (9)$$

In this equation η° represents a constant including (1) the standard potential of the $I_3^- - I^-$ couple, (2) the potential of the Ag^+/Ag reference half-cell and (3) the constant term 29.58 log $[I^-]^3$ V_{solution}. The number of moles of electrons withdrawn at the anode are denoted by μ and μ° is the symbol for the moles of manganese(III) ions which are sought for.

The most probable value for μ° was calculated in two steps. First a plot of $10^{-E_{I_3^-}/29.58}$ *versus* μ was made and the intercept on the μ-axis was determined. In the vicinity of this graphically estimated μ° value, several others were assumed and with each of them η° was calculated for every point, $E_{I_3^-}(\mu)$, of the titration. The μ° choice giving rise to an η° value constant to within 0.1 mV being accepted as the correct one.

By this method a few tenths of a μmol of triiodide ions could be determined with an uncertainty not exceeding 1 %. With 1 μmol, an accuracy of 0.1 % has been found to be easily attainable.

In this type of analysis two main difficulties are encountered. Oxygen must of course be rigorously excluded and the iodine contamination of the sodium iodide preparation must be reliably determined.

The first requirement could be fulfilled by employing for the titration an air-tight cell arrangement similar to that used for the manganese redox potential measurement, *cf.* Fig. 3. The sodium iodide solution was prepared *in situ* and oxygen was expelled with a stream of purified nitrogen which was switched off when the manganese sample had been introduced. The absence of oxygen was often controlled by letting the last solution of the titration stand overnight; during this time the redox potential change never exceeded a few tenths of an mV.

The iodine contamination of our sodium iodide sample ("specially purified" by the Merck Co., Darmstadt) was measured in blank experiments which were conducted as the manganese(III) titrations. Our sample was found to contain 1 ± 0.1 μmol of iodine per mol sodium iodide. When significant, this amount was substracted from the direct analysis result.

Some additional experiments were made to find whether any decomposition of manganese(III) might occur during the sampling. Varying the residence time of the manganese sample in the pipette from 30 s to 5 min was without effect, likewise rinsing the pipette with a few milliliters of the test solution prior to the sampling did not appreciably influence the result of the analysis. Nevertheless, rinsing was usually applied as a precaution to avoid accidental contamination.

Each series of measurements was carried out with the programmable *data acquisition system* of our laboratory. To bring our long series of measurements to a successful completion without automatization would certainly have met with great difficulties.

The E_R values with the several iridium and gold electrodes as well as the E_H data were determined with a precision of 0.01 mV by using an IDVM with 10^{10} Ω input impedance. The current supply for the electrolysis has been synchronized with a digital counter; the actual current level strength was continuously monitored by measuring with the IDVM the potential drop caused by the electrolysis along a resistance of NBS type. The current fluctuations seldom exceeded one part in 10^4. By choosing electrolysis periods long enough to make the synchronization uncertainty of around 0.01 sec, arising from the relay switchings, negligible, the number of ampere seconds passed through during an electrolysis step could always be determined with an uncertainty not exceeding 0.01 %.

RESULTS AND DISCUSSION

We have studied the five acidity levels, shown in Table 1, which cover, in about equal logarithmic steps, the interval 0.26 to 3 M. At lower hydrogen ion concentrations we have not been able to generate an amount of manganese(III) sufficient for reliable E_R measurements. The higher limit was chosen to maintain the same total molarity level at which the other triply charged ions have been previously studied in this laboratory and elsewhere.

At every H level at least two series of measurements comprising generally ten E_R determinations have been made. At each of the acidities the function $\varepsilon^\circ = e^\circ + 59.16 \log [\mathrm{Mn}^{3+}][\mathrm{Mn(III)}]^{-1}$ has proved to remain constant as the manganese(III) concentration was stepwise increased between the limits indicated in Table 1. This result shows that in these dilute manganese(III) solutions mononuclear hydrolysis products are formed only. Thus we can write

$$\varepsilon^\circ = e^\circ + 59.16 \log \frac{[\mathrm{Mn}^{3+}]}{[\mathrm{Mn(III)}]} = e^\circ - 59.16 \log (1 + \sum {}^*\beta_p H^{-p}) \tag{10}$$

Table 1. Summary of conditional standard potentials.

H M	ε° mV	Mn(III) concentration range investigated, μM
0.258	1473 ± 1	30 – 61
0.5676	1503 ± 1	32 – 63
1.000	1519 ± 1	27 – 104
1.500	1528 ± 1	34 – 104
2.968	1541 ± 0.5	40 – 287

where $^*\beta_p = [Mn(OH)_p]H^p[Mn^{3+}]^{-1}$ symbolizes the equilibrium constant for the reaction step

$$Mn^{3+} + pH_2O \rightleftharpoons Mn(OH)_p^{(3-p)+} + pH^+$$

As a consequence we may call ε° the conditional standard potential of the Mn(III)$-Mn^{2+}$ couple valid at a certain H level.

A typical series of measurements is illustrated in Table 2; each [Mn(III)] value represents the result of a iodometric analysis and each E_R datum is the mean of two redox potential determinations differing at most 0.2 mV.

In order to check the influence of accidental contamination, several series were made at each acidity levels. For instance, the three experiments at $H = 0.258$ M afforded the ε° values 1472.8, 1473.3 and 1474.1 mV whence the average included in Table 1 is calculated by taking into account the spread within the individual series as well. In the last series the reversibility was tested by building up first an [Mn(III)] of 61 μM which was then reduced stepwise to 37 μM.

The starting value of the manganese concentration was usually chosen to lie between 10 and 20 mM. In a few special experiments, measurements were made with $B_0 = 3.8$ as well as with 16.2 mM; *e.g.* at $H = 1.5$ M both series yielded the ε° value 1528 ± 1 mV. No appreciable difference in ε° was ever found when B_0 was varied between the indicated limits.

To find the composition of the hydrolysis products and the corresponding formation constants, the $\varepsilon^\circ = \varepsilon^\circ$ (log H) data have been compared with model functions representing different hypotheses. With the assumption that a single reaction product, $Mn(OH)_p^{(3-p)+}$, is formed, no fit could be achieved. Comparison with the model based on the formation of $MnOH^{2+}$ and $Mn(OH)_2^+$

$$Y = -59.16 \log(1 + v + lv^2) \equiv Y(\log v)_l \tag{11}$$

where $v = {}^*K_1\ H^{-1}$ and $l = {}^*\beta_2 {}^*K_1{}^{-2}$ yielded, however, a satisfactory agreement, as it is shown in Fig. 4. Model functions with l values ranging from 0.05 to 1 were calculated and superimposed on the ε° data. The closest fit was found with $l = 0.2$, and we read off from the magnitude of the lateral translation needed to bring the model function $Y(\log v)_{0.2}$ in coincidence with the experiments the most probable value for $\log {}^*K_1 = \log v - (-\log H)$ to equal 0.4, and from the vertical translation e°, the standard potential of $Mn^{3+} - Mn^{2+}$, to equal 1559 mV.

Table 2. An example for a series of measurements. Hydrogen ion concentration level 0.999_8 M. Initial manganese(II) concentration 7.345 mM. After the series had been terminated, manganese(III) was reduced with H_2 and E_{H_2} was determined to 645.1 mV.

E_R (iridium) mV	[Mn(III)] μM	$E_R - 59.16 \log \frac{[Mn(III)]}{[Mn^{2+}]}$
728.6	27.2	872.4
743.0	48.0	872.1
748.2	58.8	872.0
753.6	69.2	873.2
756.2	74.8	873.8

As it is illustrated in Fig. 4 the uncertainty of our ε° determinations give rise to the following limits of uncertainty

$$e^\circ = 1559 \pm 3 \text{ mV} \tag{12}$$

$$\log {}^*K_1 = 0.4 \pm 0.1 \tag{13}$$

$$\log {}^*\beta_2 = 0.1 \pm 0.1 \tag{14}$$

Eqns. (12) and (14) may be regarded as the final results of this work.

Our log $^*K_1$ value is thus seen to be in reasonable agreement with the estimates of the previous

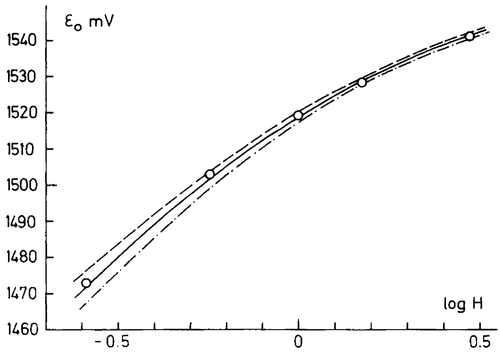

Fig. 4. The conditional standard potential, ε°, as a function of log H. The full-drawn curve represents the equation $\varepsilon^\circ = 1559 \text{ mV} - 59.16 \log(1 + 2.5H^{-1} + 1.25H^{-2})$. The broken curve corresponds to the choice $e^\circ = 1562$ mV, $\log {}^*K_1 = 0.5$ and $l = 0.1$, while the dotted curve illustrates the choice: $e^\circ = 1556$ mV, $\log {}^*K_1 = 0.3$, $l = 0.375$.

investigators[1-3] who studied such acidic solutions that the second step became much suppressed and who wanted to give only the order of magnitude of the protolysis constant for this strong acid.

In the light of the present results we have reinterpreted Wells' and Davies' spectrophotometric data[4] by assuming the magnitudes of log $^*K_1$ and of log $^*\beta_2$ in their 4 M perchlorate medium to equal our values. As the medium effect estimates of the next paragraph indicate, no serious error is likely to arise from this assumption.

The spectrophotometric data at 300 nm were recalculated to the form $\log A(1+{}^*K_1H^{-1}+{}^*\beta_2H^{-2})$ *versus* log H and they were compared with the model function $\log(1+u+lu^2)=Y(\log u)_l$. In these formulas A represents the absorbance of the manganese(III) species, u is the normalized variable $\varepsilon(\mathrm{MnOH}^{2+})\varepsilon(\mathrm{Mn}^{3+})^{-1}\,{}^*K_1H^{-1}$ and l is the parameter ${}^*\beta_2{}^*K_1{}^{-2}\varepsilon(\mathrm{Mn}^{3+})\varepsilon(\mathrm{Mn(OH)_2}^{+})\varepsilon(\mathrm{MnOH}^{2+})^{-2}$.

The best fit has been found with $l=0.03$; we derived then on the basis of the coordinate translations the molar absorptivities $\varepsilon(\mathrm{Mn}^{3+})=30$, $\varepsilon(\mathrm{MnOH}^{2+})=243$, and $\varepsilon(\mathrm{Mn(OH)_2}^{+})=308$ cm^2 mol^{-1}. The fit is illustrated in Fig. 5.

To enable us to estimate other manganese(III) equilibria, we attempted to assess the magnitude of the standard potential and that of log $^*K_1$ in the *conventional reference state:* dilute aqueous solution. Assuming the validity of the specific interaction theory and postulating the interaction coefficients of the manganese(III) and iron(III) species to be equal, we obtained that $e^\circ_{\mathrm{standard}}=1604$ mV and $\log {}^*K_{1,\mathrm{standard}} - \log {}^*K_1$ (3 M) is less than the uncertainty of our log $^*K_1$ (3 M) determination.

For the $e^\circ_{\mathrm{standard}}$ calculations we used the interaction coefficients derived in a previous communication.[8] The medium effect on log $^*K_1$ was estimated by considering the log $^*K_1(\mathrm{Fe}^{3+})$ data in 3, 1 and 0.5 M $\mathrm{NaClO_4}$ solutions.[9] The formation of $\mathrm{Fe(OH)_2}^{+}$ seems to have been studied only in 3 M $\mathrm{NaClO_4}$, so we are not able to derive a value for $\log {}^*\beta_{2,\mathrm{standard}}$.

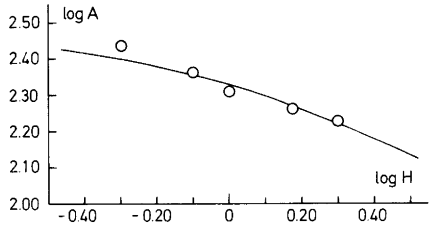

Fig. 5. Recalculation of Davies' and Wells' spectrophotometric data,[4] logarithm of the manganese(III) absorbance as a function of log H. The curve has been calculated with the log $^*K_1$ and log $^*\beta_2$ values of (13) and (14) and with the molar absorptivities of the text.

Since the radii of the triply charged cations of the 3*d* series have been estimated to vary but little, for each of them a value near to 0.65 Å has been deduced,[10] we have to seek *an explanation for the exceptional acid strength of the* Mn^{3+} *ion* on the basis of the properties of the *d* orbitals.

A correlation between the aquo acidity (as measured by log $^*K_1$) and the crystal field stabilization energy of the octahedrally coordinated $\mathrm{Me}^{3+}(\mathrm{H_2O})_6$ ions is easy to recognize. The following p$^*K_1$ values have been reported, valid, with the exception of Ti^{3+}, in a 3 M $\mathrm{NaClO_4}$ medium: Ti^{3+} 2.55 (3 M KBr medium),[11] V^{3+} 2.7,[12] Cr^{3+} 4.6,[13] Fe^{3+} 3.05[14] and Co^{3+} ≥ 2.0.[15] Titanium(III) cannot be studied at room temperature with conventional methods in this medium because it reduces $\mathrm{ClO_4}^-$ rapidly to Cl^-. The investigation of the more sluggish reducing agent V^{3+} involves also some complications and the p$^*K_1$ value cited has to be regarded as a first estimate only.

Thus Cr^{3+} with the greatest C.F.S.E. represents the weakest acid, while for V^{3+}, with only 8 Dq, $^*K_1$ is seen to be raised at least one hundred times. One would be inclined to ascribe the high p$^*K_1$ for Fe^{3+} to the special stability of a half-filled shell.

From these data we would interpolate a p$^*K_1$ value of around 2.5 to 3 for Mn^{3+} which has been shown in the present work to behave as a strong acid. This discrepancy can be made intelligible by assuming for MnOH^{2+} a ligand configuration giving rise to four low energy orbitals capable of accomodating all the *d* electrons of Mn(III). A five-coordinated $\mathrm{MnOH}^{2+}(\mathrm{H_2O})_4$ ion with the ligands in the square pyramid arrangement and with the OH^- ion near to the high-level orbital, satisfies this requirement and it provides a greater C.F.S.E. than the octahedral coordination.

Postulating the same structure for the other MeOH^{2+} ions of the series a parallelism arises between log $^*K_1$ and the difference in C.F.S.E. for the square pyramid and the octahedral coordination. For this difference the following estimates have been made by Basolo and Pearson[16] (who intended to explain kinetic data but have realized the potential value of their calculations for the interpretation of equilibria) Mn^{3+} 3.14, V^{3+} 1.14, Co^{3+} and Ti^{3+} 0.57, Fe^{3+} zero, Cr^{3+} -2.00. Hence we may have little doubt that the hydrolysis of these ions is greatly influenced by ligand field effects.

On the basis of these speculations we may expect the Mn^{3+} ion to form complexes of extraordinary strength not only with OH^- but also with other singly charged anions. Equilibria of this type are now being studied in this laboratory and the results will form the subject of a forthcoming publication.

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