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A Spectrophotometric Study of Tripositive Manganese in Hydrochloric Acid Solution[1a]

BY JAMES A. IBERS AND NORMAN DAVIDSON[1b]

Introduction.—When a solution of manganese (II) in hydrochloric acid is oxidized with a suitable oxidizing agent, or when manganese dioxide or potassium permanganate is dissolved in hydrochloric acid, a deep brown-red color is produced; the investigations described here are concerned with the identification of the species responsible for this color.

A review of the extensive and controversial early literature on "the higher manganese chlorides" is given by Mellor.[2] It has generally been supposed that chloro-complexes of either manganese(III) or manganese(IV) or of both oxidation states are present in the colored solutions. However, it has not been possible heretofore to state with certainty how much of each oxidation state is present in a particular solution. The higher chlorides of manganese are unstable in hydrochloric acid solution and decompose to the manganese(II) state with the evolution of chlorine,[3]

$$Mn^{II+n} + nCl^- = Mn^{++} + (n/2)Cl_2 \qquad (1)$$

Because of this decomposition, it is difficult to ascertain how much of the oxidizing capacity of a solution is due to chlorine and how much to manganese compounds; and it is difficult to ascertain how much of the manganese in a solution is in the dipositive state and how much in higher states.

Weinland and Dinkelacker[4] have obtained solid compounds of both tripositive and tetrapositive manganese, *e. g.*, K_2MnCl_6, K_2MnCl_5, Rb_2MnCl_6, Rb_2MnCl_5, by treatment of permanganate solutions with concentrated hydrochloric acid; Meyer and Best[5] have prepared similar substances by the reduction of potassium permanganate with acetic acid followed by the addition of hydrogen chloride. Only the tripositive compounds, $M_2Mn^{III}Cl_5$, have been obtained after dissolving manganese dioxide in concentrated hydrochloric acid.[6,7] Because of the effects of solubility in shifting equilibria, these precipitates are not necessarily indicative of what oxidation states are present in the solutions.

We may note in passing that the claim by Chrétien and Varga[8] to have prepared pure manganese trichloride by the action of liquid hydrogen chloride on manganese triacetate at −100° cannot be regarded as proven. In the preparation, excess hydrogen chloride and volatile reaction products were removed by evacuation at −60°; it is unlikely that acetic acid, if formed, could be pumped off at this temperature. The analyses reported by these authors do not demonstrate the absence of acetic acid of crystallization.

Pickering[9] and Sem[10] have given the most convincing evidence for the occurrence of tripositive manganese in hydrochloric acid solution. Sem analyzed oxidized manganese solutions by dilution with excess water; manganese (III) and (IV) are assumed to react by equations (2) and (3), respectively.

$$2Mn^{III} + 2H_2O \longrightarrow Mn^{++} + MnO_2 + 4H^+ \qquad (2)$$

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

He observed in the electrolytic oxidation of solutions of manganese(II) chloride in 7 *F* hydrochloric acid at −10° a limiting yield of oxidized manganese of either 100% manganese(III) or 50% manganese(IV), thus indicating that manganese(III) was formed. At higher temperatures (*ca.* 20°) only about 75% of manganese(III) could be produced, because the rate of reaction (1) in the forward direction was comparable with the rate of electrolytic oxidation. Campbell[11] also observed the electrolytic formation of a higher manganese chloride; his argument that this was the tetrapositive state is not valid. Pickering[9] distinguished between the oxidizing capacity of a solution due to free chlorine and that due to oxidized manganese; (a) by reaction (2), and (b) by removing dissolved chlorine in a current of air. He found that as a limiting case approached at low temperatures (−10°), one mole of manganese dioxide dissolves in hydrochloric acid to liberate one equivalent of free chlorine, that is, according to the equation

$$MnO_2 + 4H^+ + Cl^- \longrightarrow {}^1/_2Cl_2 + Mn^{III} + 2H_2O \qquad (4)$$

At higher temperatures, more chlorine is liberated. Less chlorine is liberated if the dioxide is dissolved in a solution containing manganese(II)

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(1) (a) Presented as a part of a contribution to the Symposium on "Unfamiliar Valence States of Familiar Elements" at the 117th Meeting of the American Chemical Society, Detroit, Mich., April, 1950; (b) responsible co-author.

(2) J. W. Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. XII, Longmans, Green, and Co., London, New York and Toronto, 1932, pp. 374–380.

(3) For the chemical equations in this paper, we have chosen to write Mn^{III} (or Mn^{IV}) instead of Mn^{+++} because tripositive manganese is strongly complexed by chloride but to an unknown extent in the solutions studied. Dipositive manganese is probably less strongly complexed by chloride in these solutions and we write the conventional Mn^{++} for this species. For consistency, the equations are balanced with respect to H^+, Cl^-, etc., as though Mn^{III} were Mn^{+++}.

(4) Weinland and Dinkelacker, *Z. anorg. Chem.*, **60**, 173 (1908).

(5) Meyer and Best, *ibid.*, **22**, 185 (1900).

(6) Neumann, *Monatsh.*, **15**, 492 (1894); *Chem. Centr.*, **65**, II, 939 (1894).

(7) Rice, *J. Chem. Soc.*, **73**, 258 (1898).

(8) Chrétien and Varga, *Bull. soc. chim. France*, [3] **3**, 2385 (1936).

(9) Pickering, *J. Chem. Soc.*, **35**, 654 (1879).

(10) Sem, *Z. Elektrochem.*, **21**, 426 (1915).

(11) Campbell, *J. Chem. Soc.*, **123**, 892 (1923).

TABLE I

VALUES OF $D(\lambda)/[\mathrm{Mn}^{++}][\mathrm{Cl}_2]^{1/2}_{\mathrm{CCl}_4}$ FOR SOLUTIONS OF Mn^{++} OXIDIZED BY Cl_2 AT 25.3°

Wave length, λ	IA	IB	IIA	IIB	IIIA	IIIB	IVA	IVB	Av.[d]
625 mμ	10.8	11.4	11.0	10.9	11.2	11.1	10.5	10.5	10.9
600	14.7	15.3	15.0	15.3	15.4	15.1	14.7	14.6	15.0
575	17.4	18.0	17.5	17.3	17.7	17.4	16.7	17.0	17.4
550	17.4	18.2	17.7	17.4	18.2	17.5	17.1	17.3	17.6
525	16.6	17.4	17.0	16.8	17.3	16.6	16.4	16.4	16.8
500	18.0	19.1	18.4	18.1	18.8	18.4	18.0	18.0	18.4
Composition of Solutions									
$[\mathrm{Cl}_2]^a_{\mathrm{CCl}_4}$	0.975	0.194	0.135	0.880	0.940	0.212	0.102	0.720	
$[\mathrm{Mn}^{++}]^{a,b} \times 10^2$	9.34	9.74	9.69	9.44	3.20	3.28	3.30	3.14	
$[\mathrm{Mn}^{\mathrm{III}}]^{a,c} \times 10^3$	5.2	1.2	1.7	4.2	1.5	0.70	0.50	2.1	
$[\mathrm{HCl}]^a$	10.1	10.1	10.2	10.2	10.2	10.2	10.1	10.1	

[a] Units of moles/liter. [b] Corrected for the concentration of $\mathrm{Mn}^{\mathrm{III}}$. [c] Calculated from the extinction coefficients of $\mathrm{Mn}^{\mathrm{III}}$ measured subsequently. [d] Average deviations vary from 0.2 to 0.3.

ions; in the limiting case, the reaction is

$$4\mathrm{H}^+ + \mathrm{MnO}_2 + \mathrm{Mn}^{++} \longrightarrow 2\mathrm{Mn}^{\mathrm{III}} + 2\mathrm{H}_2\mathrm{O} \quad (5)$$

Vernon[12] has claimed however that at −26°, manganese dioxide dissolves in hydrochloric acid to give manganese(IV) and no chlorine; his work has been questioned by Pickering.[13]

The investigations described below show that when manganese(II) in solution in hydrochloric acid is oxidized by chlorine, the coloration is due to manganese(III) only; and that it is possible to measure the equilibrium constant for the reversible reaction

$$\mathrm{Mn}^{++} + \tfrac{1}{2}\mathrm{Cl}_2 = \mathrm{Mn}^{\mathrm{III}} + \mathrm{Cl}^- \quad (6)$$

Experimental.—To prepare manganese(II) solutions, C. P. $\mathrm{MnCl}_2\cdot 4\mathrm{H}_2\mathrm{O}$ was dissolved in hydrochloric acid. The acid concentrations of these solutions were measured by titrations with standard base to a brom phenol blue endpoint. The manganese(II) was determined by a potentiometric titration with standard permanganate to give the tripositive manganese pyrophosphate complex.[14] Before the titration the manganese(II) solution in concentrated hydrochloric acid was evaporated to a small volume and diluted with water to reduce the chloride concentration. The permanganate solution was prepared with the usual precautions and standardized against sodium oxalate.[15]

The total oxidizing capacity of a solution was determined by running it into excess potassium iodide solution and titrating the liberated iodine with thiosulfate solution (standardized against potassium dichromate). These titrations were performed either in an acetate buffer or under an atmosphere of carbon dioxide to avoid an "oxygen error."

The C. P. carbon tetrachloride used was stated to have less than 0.01% of reducing substances; however it partially decolorized oxidized manganese solutions. To avoid this it was pretreated with chlorine for twenty-four hours. The chlorine could be removed by refluxing.

Absorption spectra were obtained with a Beckman Model DU quartz spectrophotometer, using 1.00-cm. capped quartz or Corex cells. The optical density, D, reported here is equal to $\log_{10} I_0/I$. Extinction coefficients are defined by $\epsilon = D/cl$, where l is the light path in centimeters and c is the concentration of the absorbing solution in volume molal units.

The Oxidation of Manganese(II) with Chlorine at 25°.—It was proposed to determine whether there was an equilibrium optical density for a manganese(II) solution in concentrated hydrochloric acid oxidized by a fixed concentration of chlorine. In the absence of a catalyst, the color of such a solution develops slowly and continues to increase even after several weeks. Bobtelsky and Cohen[16] discovered that for a higher manganese chloride prepared by the addition of potassium permanganate solution to aqueous hydrochloric acid, reaction (1) in the forward direction is catalyzed by various dissolved substances, including silver(I), copper(II), platinum(IV), and lead(II). Following this lead we have discovered that silver(I) may be used as a catalyst to achieve the equilibrium state for reaction (1).

The procedure was: to a hydrochloric acid solution containing manganese(II), small quantities of a concentrated silver nitrate solution were added to give 10^{-3} to 10^{-2} F Ag^{I}. About 20 ml. of this solution was equilibrated with about 50 ml. of a solution of chlorine in carbon tetrachloride in a sealed vessel in a 25.3° thermostat. Since chlorine is more soluble in carbon tetrachloride than in the aqueous phase, this technique provides a large reservoir of chlorine at a fixed activity. Furthermore, since the higher manganese chloride is insoluble in the organic phase, the oxidizing titer of this phase is a direct measure of the chlorine activity. At the end of the equilibration period, the absorption spectrum of the aqueous phase was measured; at the same time, the chlorine content of the carbon tetrachloride phase was determined by titration. With 10^{-2} F Ag^{I} as a catalyst, only four hours were required for equilibrium; with 10^{-3} F Ag^{I}, about twenty-four hours were used. The lower catalyst concentration was adopted for the measurements reported here, because then the rate of decomposition of the higher manganese chloride was slow enough not to interfere with the spectrophotometric measurements made shortly after separating the aqueous phase from the carbon tetrachloride phase.

Table I presents a typical set of results. The quantity recorded is $(D(\lambda)/[\mathrm{Mn}^{++}][\mathrm{Cl}_2]^{1/2}_{\mathrm{CCl}_4})$. The quantity D is the observed optical density of the solution, $[\mathrm{Cl}_2]_{\mathrm{CCl}_4}$ is the chlorine concentration (moles/liter) in the carbon tetrachloride phase, and $[\mathrm{Mn}^{++}]$ is the final concentration of manga-

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[12] Vernon, *Phil. Mag.*, **31**, 469 (1891).

[13] Pickering, *ibid.*, **33**, 284 (1892).

[14] Lingane and Karplus, *Ind. Eng. Chem., Anal. Ed.*, **18**, 191 (1946).

[15] Fowler and Bright, *J. Research Natl. Bur. Standards*, **15**, 493 (1935).

[16] Bobtelsky and Cohen, *Compt. rend.*, **201**, 662 (1935)

nese(II) in the aqueous phase. The latter concentration is slightly different from the total manganese concentration because of the manganese(III) present. The method used for determining the manganese(III) concentration is described later. The runs labelled "A" were started with unoxidized manganese(II) solutions; the "B" runs initially contained the oxidized manganese solutions from the "A" runs, but a different chlorine concentration.

The result of Table I that D is proportional to the product $[Mn^{++}][Cl_2]^{1/2}$ *implies that the colored species is* Mn^{III} *formed in equilibrium amounts according to equation* (6). (Light absorption by chlorine is negligible in these solutions.) It is to be emphasized that in Table I this equilibrium has been approached from both higher and lower values of $[Mn^{III}]$ than the equilibrium value for a particular solution.

At a fixed hydrochloric acid concentration, we may write a mass-action equilibrium constant for reaction (6)

$$K = [Mn^{III}]/[Mn^{++}][Cl_2]^{1/2} \qquad (7)$$

In equation (7), $[Cl_2]$ is the chlorine concentration in the aqueous phase. Both manganese(II) and manganese(III) are probably complexed by chloride to an extent that varies with the hydrochloric acid concentration; it is not possible to predict therefore how K of equation (7) will vary with the acid concentration and there is no point in writing a more general equilibrium constant which contains the activity of hydrochloric acid as a factor.

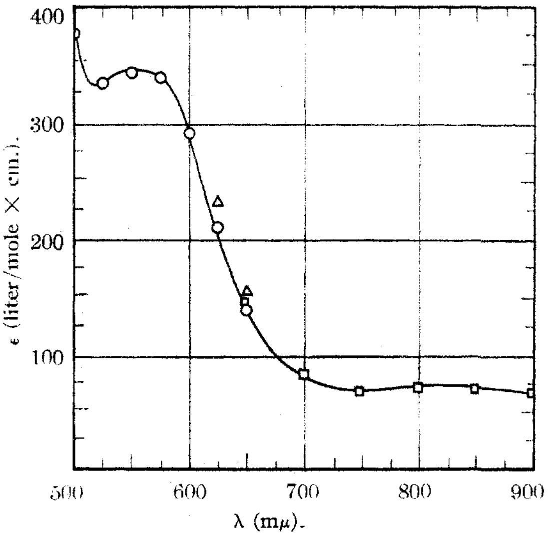

Fig. 1.—Absorption spectrum of manganese(III) in 10.0 F hydrochloric acid: O, 2.94×10^{-3} F Mn^{III}; △, 4.63×10^{-3} F Mn^{III}; □, 3.12×10^{-3} F Mn^{III}. This last concentration was determined spectrophotometrically from the optical density of the solution at 600 mμ. The curve is drawn through the O points rather than the △ points because the former points were checked several times with solutions of approximately the same composition.

The distribution ratio of chlorine between carbon tetrachloride and 9.8 or 10.1 F hydrochloric acid containing 0.0 to 0.1 F Mn^{++} was determined to be 15.5 ± 0.1 at 25°. (During the distribution experiments no appreciable amount of Mn^{III} was formed.)

The extinction coefficients of manganese (III) in 10.0 F hydrochloric acid were measured by determining both $[Mn^{III}]$ and D for some solutions prepared by chlorine oxidation of manganese(II) with no silver catalyst present. These solutions were not necessarily at equilibrium with respect to reaction (6). The absorption spectra were measured. Free chlorine was now rapidly extracted with pure carbon tetrachloride, using a separatory funnel. Two extractions of an aqueous phase with about twice the volume of carbon tetrachloride were sufficient; since there was no measurable oxidizing matter in the third extract, the reaction (6) in the backward direction was not taking place to an appreciable extent during the five minute periods involved. The oxidizing capacity of the aqueous phase was now immediately determined; this was due to tripositive manganese. Figure 1 displays the extinction coefficients of manganese(III) measured in this way.

These results in conjunction with the data of Table I and the measured distribution coefficient of chlorine imply a value of K for equation (7) in 10.1–10.2 F hydrochloric acid of 0.190 (±0.004) $(\text{liter/mole})^{1/2}$.

In a series of measurements like those of Table I at an acid concentration of 9.8 F the values of $D/[Mn^{II}][Cl_2]^{1/2}{}_{CCl_4}$ were about 8% less than those of Table I. No effort was made to ascertain the relative contributions of a change in the equilibrium constant of equation (6) and a change in the extinction coefficients of manganese(III) to this decrease.

Reaction (6) at 0°.—Solutions of 0.10 F manganese(II) in 10 F hydrochloric acid were equilibrated with a chlorine–carbon tetrachloride phase in an ice-bath for one to two week periods. The aqueous solutions were then analyzed for manganese(III) by the titration method after rapid removal (~2–3 min.) of free chlorine by two extractions with carbon tetrachloride. Some silver ion was present as a catalyst; in order to avoid rapid decomposition of the manganese(III) during the extractions, the catalyst concentration was rather low. Table II presents the results of these measurements. The calculated equilibrium constants in the table are based on the measured distribution coefficient for chlorine between carbon tetrachloride and 10.0 F hydrochloric acid at 0° of 13.1.

TABLE II

OXIDATION OF MANGANESE(II) BY CHLORINE AT 0°

Expt. no.	1[b]	2[b]	3[b]	4[b]	5[b]	6[c]
$[Cl_2]_{CCl_4}$	0.650	1.52	1.51	1.02	2.88	1.13
$[Ag^I] \times 10^4$	2.5	25	50	0.94	0.94	0.94
$[Mn^{III}] \times 10^3$	7.0	10.9	11.2	7.2	12.7	9.6
K[a]	0.29	0.30_5	0.31	0.24	0.26	0.33_6

[a] Calculated by equation (7). [b] Seven day equilibration time. [c] Fifteen day equilibration time; for run (6) part of the aqueous solution from run (5) was sealed in a tube with a different (and less concentrated) solution of Cl_2 in CCl_4.

For experiment (1), the manganese (III) titer was determined by a thiosulfate titration at 0°. Because the starch–triiodide complex is not rapidly decomposed by excess thiosulfate, this end-point was judged by the disappearance of the triiodide color itself; the titration may therefore not be as accurate as some of the others. For experiments (2) and (3) with the high catalyst concentration, the manganese(III) in the aqueous solutions decomposed about 30% in ten minutes, as indicated by carbon tetrachloride extraction at this time. This implies a 5–10% decomposition during the time required for the initial extraction. This rather uncertain correction for the concentration of manganese(III) has not been made for the data in Table II. Solution (4) with a much lower catalyst concentration decomposed 20% in fifteen minutes, indicating less than 5% decomposition during the extraction time for this run, and presumably also for runs (5) and (6). Probably the low values of K for runs (4) and (5) are due to insufficient equilibration time at the low catalyst concentration. It is noteworthy that the final manganese(III) concentration for run (6) is lower than that of the initial solution (from run (5)); thus the equilibrium has been approached from both sides.

It is evident from the discussion of the preceding paragraph that the results of Table II do not yield a very accurate value for the equilibrium constant. However, the general agreement of experiments (1), (2), (3) and (6) indicates that the function K of equation (7) is indeed a constant. The main oxidation product is therefore still manganese(III), not manganese(IV), and the equilibrium constant for equation (6) at 0° has the value 0.33 ± 0.03. The decrease in K by a factor of 0.58 in going from 0 to 25° corresponds to a calculated ΔH (assumed to be temperature independent) for reaction (6) of -3.7 kcal.

Absence of Interaction Absorption in the Manganese(II)–Manganese(III) System.—The original impetus for this research was our anticipation that the strong color of oxidized manganese(II) solutions in hydrochloric acid might prove to be non-additive light absorption due to the presence of manganese in several oxidation states. Other cases of interaction absorption in solution have been studied in this Laboratory.[17] If this were the case, the optical density of the oxidized solutions would obey a law of the type $D = k_{\text{int.}}(\lambda)[\text{Mn}^{++}][\text{Mn}^{\text{III}}]$. Table I shows that this is not the case in the wave length range 500–625 mμ.

That interaction absorption is not responsible for the coloration in the 600–900 mμ range was shown in the following experiment. A 1.0 F manganese(II) solution in 10.4 F hydrochloric acid was oxidized with chlorine for several weeks so that it became strongly colored and so that the color no longer changed appreciably with time. The solution had an optical density of 0.920 at 650 mμ and of 0.395 at 900 mμ. It was diluted by a factor of 2 with a saturated solution of chlorine in hydrochloric acid, and the resulting solution was again diluted by a factor of 2 with the same diluent. There was presumably no oxidation or reduction of the manganese during these dilutions. After the first dilution, the optical densities at all wave lengths fell by a factor of 1.9, and after the second dilution by a factor of 1.8. The reason for the deviation of these factors from 2.0 is not known, but it is quite clear that each twofold dilution did not cause a fourfold decrease in the optical density as is predicted by the interaction absorption hypothesis.

Mixed ferrous–ferric solutions in concentrated hydrochloric acid exhibit the phenomenon of interaction absorption.[18] Probably interaction absorption in hydrochloric acid solution can occur only when both oxidation states form chloro-complexes.[17,18] The difference in the behavior of the iron and the manganese solutions may then be explained by the hypothesis that the amount of complexing of manganese(II) by chloride is less than the amount of complexing of iron(II) by chloride. In general, iron(II) forms stronger complexes than manganese(II).[19] It is pertinent to point out that the interaction absorption for the iron(II, III) system is much less marked than the interaction absorption for the copper(I, II) or antimony(III, V) system. The still weaker interaction absorption predicted by the above argument for the manganese(II, III) system might well not be observable. That there is probably some complexing of manganese(II) by chloride in 5.7 and 11.4 F hydrochloric acid is shown by the fact that manganese(II) in these solutions is more strongly absorbing in the ultraviolet region of the spectrum than manganese(II) chloride dissolved in water. Some observations on this point are recorded in Table III. The limited data do not allow one to infer the formulas and stabilities of the chloro-complexes responsible for the light absorption. The qualitative observation that the color of a 1 F manganese(II) chloride solution in concentrated hydrochloric acid is yellow pink as compared to the pink color of a concentrated solution of manganese(II) nitrate in water also suggests the formation of chloro-complexes.

TABLE III

ABSORPTION SPECTRA OF MANGANESE(II) IN HYDROCHLORIC ACID SOLUTIONS

$[\text{Mn}^{++}]$	0	0.1	0.2	0.2
[HCl]	11.7	5.7[a]	11.4	0
λ(mμ)	Optical densities, D			
230	0.185	1.16	2	0.100
235	0.16	0.595	1.7	0.05
240	0.13	0.38	0.635	0
245	0.11	0.30	0.28	0
250	0.10	0.27	0.20	0

[a] Hydrochloric acid solutions of this concentration are colorless.

The Reaction of Permanganate with Manganese(II) and Hydrochloric Acid.—Bobtelsky and Cohen[16] reported that when permanganate is added to an excess of manganese(II), in hydrochloric acid, the ratio of the number of equivalents of free chlorine formed to the number of equivalents of a higher manganese chloride is one. This would suggest a single simple reaction path. We have briefly studied this subject and find that the ratio defined above is variable, depending on the experimental conditions.

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(17) Whitney and Davidson, THIS JOURNAL, **71**, 3809 (1949); McConnell and Davidson, *ibid.*, **72**, 3168 (1950).

(18) McConnell and Davidson, *ibid.*, **72**, accepted (1950).

(19) Irving and Williams, *Nature*, **162**, 746 (1948); Mellor and Maley, *ibid.*, **161**, 436 (1948); **159**, 370 (1947).

Table IV displays the results obtained. The experiments were performed by mixing the reagents in aqueous solutions in a separatory funnel containing 50 ml. of carbon tetrachloride, shaking vigorously immediately after mixing, and then separating the two phases. The manganese(III) (and higher oxidation states if they be present in these nonequilibrium solutions) and free chlorine concentrations were determined iodometrically; a distribution coefficient of 15 for chlorine between the organic and aqueous phases was used.

TABLE IV

REACTION OF PERMANGANATE WITH MANGANESE (II) AND HYDROCHLORIC ACID AT 25°

$[MnO_4^-]$[a] $\times 10^3$, moles/liter	$[Mn^{++}]$[a]/ $[MnO_4^-]$	[HCl][a] moles/ liter	Vol. aq. phase, ml.	$\frac{\text{Equiv. } Cl_2}{\text{Equiv. } Mn^{III}}$ B[b]	C[b]
9.9	5.1	5.0	20	0.65	0.64
9.4	10.1	5.2	21	.39	.28
10.0	8.0	6.0	50	1.0	
4.0	0	8.0	15		3.0
3.0	9.8	8.5	20	1.6	1.7
2.1	14.7	8.9	19	1.7	1.3

[a] Calculated initial concentrations after mixing, but before reaction. [b] Procedure B, 0.02 *F* MnO_4^- soln. added through the CCl_4 phase to the Mn^{++} in HCl soln.; procedure C, Mn^{++} in HCl added through the CCl_4 phase to the 0.02 *F* MnO_4^- soln.

The results in Table IV indicate that the ratio of equivalents of free chlorine to equivalents of manganese(III) produced depends on the manganese(II)–permanganate ratio, on the acid concentration, and to some extent on the order of mixing. The result in 6 *F* acid is the same as that reported by Bobtelsky and Cohen[16] in acid of this concentration with somewhat different manganese concentrations. As expected, a high ratio of chlorine to manganese(III) is obtained when permanganate is added to hydrochloric acid alone. Probably the results of experiments like these are dependent on several variables (rates of mixing, absolute concentrations, etc.) not investigated by us. We are offering the data of Table IV merely to indicate the order of magnitude of the results and to indicate that a one-to-one ratio of free chlorine to manganese(III) is not generally obtained.

Acknowledgments.—We are indebted to the Office of Naval Research for support of this work and to Professor Dan H. Campbell for many kindnesses in connection with the use of the spectrophotometer.

Summary

The equilibrium optical density, due to a higher manganese chloride, of a solution of manganese(II) in concentrated hydrochloric acid oxidized by chlorine obeys the relation $D = K\epsilon[Mn^{++}]\cdot[Cl_2]^{1/2}$, implying that the colored species is a chloro-complex of manganese(III) formed by the reaction $Mn^{++} + {}^1/_2Cl_2 = Mn^{III} + Cl^-$. The extinction coefficients of manganese(III) were measured, and the equilibrium constant, $K = [Mn^{III}]/[Mn^{++}][Cl_2]^{1/2}$ (liter/moles),$^{1/2}$ in 10.1 *F* hydrochloric acid was evaluated as 0.19 (25°) and 0.33 (0°).

There is no optical interaction absorption in mixed solutions of manganese(II) and (III). Spectrophotometric evidence for the formation of chloro-complexes of manganese(II) is presented. The ratio of the amount of tripositive manganese to the amount of chlorine formed by the reaction of permanganate with a manganese(II) solution in hydrochloric acid has been investigated.

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[CONTRIBUTION NO. 80 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TENNESSEE]

The Properties of Benzhydrol in Sulfuric Acid Solution

BY CLARK M. WELCH AND HILTON A. SMITH

When triphenylcarbinol is dissolved in sulfuric acid it ionizes according to the equation

$$(C_6H_5)_3COH + 2H_2SO_4 \longrightarrow (C_6H_5)_3C^+ + H_3O^+ + 2HSO_4^-$$

This ionization is demonstrated by the light absorption of the solution,[1] by the molar freezing point depression which is four times that caused by a non-ionized solute,[2] and by the reaction of the carbonium ions in the sulfuric acid solution with alcohols to form ethers.[3]

These characteristics naturally led to interest in the behavior of benzhydrol (diphenylcarbinol) when dissolved in sulfuric acid. The solutions are reddish-brown in color, indicating the presence of carbonium ions. Fuson and Jackson[4] reported that when such a solution was poured into cold methanol, and treated in the usual manner, no benzhydryl methyl ether was found, but two unidentified products were obtained. One of these was a liquid boiling at 178–182° (16 mm.), while the other was a hard resin at ordinary temperatures. The combined weight of these fractions was less than 50% of the weight of benzhydrol used. These same workers found that when dimesitylcarbinol was dissolved in sulfuric acid, a deep red solution resulted, and that essentially quantitative yields of dimesityl-

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(1) A. Hantzsch, *Ber.*, **54**, 2573 (1921).

(2) A. Hantzsch, *Z. physik. Chem.*, **61**, 257 (1908); L. P. Hammett and A. J. Deyrup, THIS JOURNAL, **55**, 1900 (1933).

(3) H. A. Smith and R. J. Smith, *ibid.*, **70**, 2400 (1948).

(4) R. C. Fuson and H. L. Jackson, *ibid.*, **72**, 351 (1950).