CXCVIII.—*The Reaction between Manganese Salts and Sodium Hypochlorite in the Presence of certain other Salts.*

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FROM a solution of a manganese salt sodium hypochlorite precipitates hydrated manganese dioxide, and, on prolonged boiling, a small quantity of sodium manganate or permanganate is formed. If the reaction takes place in the presence of copper salts, however, the copper is precipitated and permanganate is the main product. The latter reaction was studied by Duyk (*Ann. Chim. anal.*, 1907, **12**, 465), who gave no data, but stated that the reaction was complete for small quantities of manganese. Heslinga (*Chem. Weekblad*, 1922, **19**, 274) used bromine water in alkaline solution in place of hypochlorite, and stated that the reaction was suitable for qualitative purposes only.

It has been found that a small amount of sodium permanganate is formed even when special precautions are taken to purify both the manganese salt and the sodium hypochlorite, so the manganese dioxide itself appears to be capable of catalysing the reaction. When present in quantities roughly equivalent to that of the manganese salt, the salts of several metals, notably copper, cobalt, nickel, and molybdenum (as molybdate), possess the property of greatly increasing the amount of permanganate formed in this reaction, and the present communication is a study of the effect of variations in the conditions of the experiment on the conversion of manganese salt into permanganate.

EXPERIMENTAL.

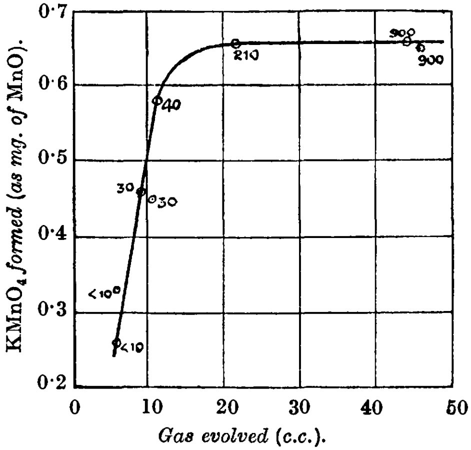
Influence of Time.—Of the oxygen available from the hypochlorite, some is utilised in the formation of permanganate, whilst the bulk is evolved as gas. The relations were observed between time of heating, permanganate formation, and evolution of gas at a temperature of 100°.

The reactants were mixed at 100° by sharply shaking a small tube, which contained measured amounts of manganese- and copper-salt solutions, and which stood normally in an upright position inside the reaction tube containing the hypochlorite. After being heated for a definite time, the reaction tube was immersed in an ice-bath, the volume of gas evolved was measured, and the permanganate estimated colorimetrically. Only at 100° is the suspension of copper oxide sufficiently agitated, without the use of a stirrer, to exert a constant and maximum influence on the reaction. But since the reaction has been chiefly studied at this temperature, no attempt has been made to carry out the above experiment at any other temperature. The results were as follows, *all weights of manganese salts and permanganates being expressed, both here and later, as mg. of* MnO :

Time of boiling (secs.)	<10	<10	30	30	40	210	900	900
Volume of gas (c.c.)...	5·4	5·4	10·7	9·4	11·2	21·7	43·8	45·6
$KMnO_4$..................	0·26	0·33	0·45	0·46	0·58	0·66	0·66	0·65

These results are shown graphically in Fig. 1, and it is evident that, at these concentrations, the maximum amount of permanganate is formed at the end of about 3 minutes' boiling, and after the evolution of one-third of the total oxygen.

FIG. 1.



(*Figures near points indicate time of boiling in seconds.*)

Effect of Alkali.—On filtering the above reaction mixtures, it was noticed that the solutions sometimes had a slight bluish tint which made colorimetric comparison with permanganate solution impossible. This was very marked when the bulk of the hypochlorite had been decomposed and the ratio of alkali to hypochlorite had greatly increased. On keeping indefinitely, the solution turned greenish-blue in colour, and a brown precipitate formed. When the filtrate from this solution was treated with acid, the original pink colour was restored, with co-precipitation of manganese dioxide. The colour was found to be due to the formation of a little manganate by the action of sodium hydroxide on the permanganate.

Heslinga (*loc. cit.*) stated that the presence of iron was prejudicial to the reaction, since it caused the colour of the solution to change to bluish-violet, probably through the formation of unstable potassium ferrate. It was found, however, that (1) the bluish-violet colour was observed when no iron was present, (2) this colour formed more readily as the concentration of alkali increased, and (3) the brown precipitate contained manganese, but no iron.

Of the reagents usually employed to convert manganate to permanganate, sodium bicarbonate was found to be the only one suitable in this case, provided that sufficient hypochlorite was also present.

Extent of Reaction.—Another series of tests was carried out to discover how far the oxidation of the manganese to permanganate was quantitative, starting with different quantities of reactants.

Approximately equivalent measured amounts of manganese and of cobalt or copper salt were poured into a conical flask, and the solution was diluted to 50 c.c. To the warm solution, 10 c.c. of 5*N*-sodium hypochlorite (total alkalinity 0·1*N*) were added gradually, the flask being shaken simultaneously, and the mixture was heated. After reaching brisk effervescence, the solution was boiled for 3 minutes, a further 5 c.c. of hypochlorite were added, and the solution was again heated until it effervesced freely. After filtration through pure asbestos, the solution was cooled, made up to a known volume, and estimated colorimetrically.

I. $KMnO_4$ calc.	0·36	0·73	1·46	2·05	2·19	2·55	2·92	3·66	4·38
II. $KMnO_4$ formed :									
A. Using cobalt.	0·30	0·45	0·91		1·25		1·42		1·80
	0·30	0·46	0·93				1·44		
		0·45					1·47		
B. Using copper.		0·73	1·33	1·64	1·62	2·21	2·39	3·00	3·83
				2·00	1·87	2·50	2·58	3·06	
					2·21	2·50			
					1·98				

From the results obtained it is seen that, when cobalt is used, the ratio of permanganate formed to that theoretically possible decreases in a regular manner as the amount of manganese salt used increases. In the case of copper, however, although the amount of permanganate formed approached the theoretical more closely than when cobalt was used, the results obtained were erratic. Occasionally, the manganese was completely converted into permanganate, and it was noticed that this happened only when the standard manganese solution (in this case prepared from permanganate) was slightly acidic. It was found impossible, however, to reproduce these conditions, as a very slight excess of acid over the alkali present in the hypochlorite caused decomposition to set in, whereas a deficiency of acid did not favour complete oxidation of manganese.

These indications that low alkalinity is a critical factor in the reaction find support on theoretical grounds. Kauffmann (" Bleichlaugen und Bleichverlauf," *Z. angew. Chem.*, 1924, **37**, 364) states that the activity of sodium hypochlorite is due to free hypochlorous acid, and that the condition of higher instability occasioned by a minimal alkali content is also that of enhanced activity. Again, assuming that it is peroxide of copper that catalyses the reaction (and later observations seem to warrant this assumption), an appreciable hydroxyl-ion concentration would hasten its decomposition.

In view of the difficulty experienced in establishing and maintaining approximate neutrality during the course of the reaction by means of mineral acid, use was made of the solution of the double carbonate of sodium and copper (Aldridge and Applebey, J., 1922, **121**, 238), which has a very slight alkalinity. Owing to the buffer action of this solution, the addition of the alkaline hypochlorite does not appreciably alter the p_H value of the solution.

2 C.c. of a solution containing 100 g. of anhydrous sodium carbonate and 40 g. of sodium bicarbonate per litre were warmed to 50°, and 3 c.c. of copper sulphate solution (containing 1 g. of CuO per litre) were added. Into this solution was poured quickly a measured quantity of manganese salt solution, the liquid shaken, and, before any signs of turbidity appeared, 5 c.c. of 5*N*-sodium hypochlorite were added from a burette, whilst the flask was shaken. The liquid was diluted to 50 c.c., gently heated until freely effervescing, and then boiled for 3 minutes. Filtration through an asbestos–glass wool filter was followed by the addition of 1 c.c. of hypochlorite and 0·5 c.c. of saturated sodium bicarbonate solution. The solution was then cooled, made up to a known bulk, and the permanganate estimated colorimetrically.

	I.	II.	III.	IV.	V.	VI.	VII.
Manganese salt present	1·02	2·04	3·07	4·00	4·00	4·00	5·11
Permanganate formed	1·08	2·09	3·17	4·01	3·93	4·02	5·16

If the hypochlorite is not added immediately after the manganese salt has dissolved in the double sodium copper carbonate solution, the solution becomes turbid, and the amount of permanganate subsequently formed is decreased, as shown by the following figures (VIII—XII).

	VIII.	IX.	X.	XI.	XII.	XIII.	XIV.
Manganese salt taken	2·04	2·04	3·06	3·07	3·07	4·00	4·00
Permanganate formed	1·86	1·73	2·80	2·85	2·81	3·79	3·89

A somewhat lower result for permanganate was also obtained if only 1 minute's boiling (instead of the usual 3 minutes) was given after reaching the stage of free effervescence (Nos. XIII and XIV).

When the modified procedure described above was applied to cobalt, considerably less permanganate was formed and appreciable quantities of cobalt remained in solution, rendering colorimetric estimation difficult, owing to the difference in tint between the standard and the sample.

The filtrates I—VII were tested for copper. They were evaporated to dryness and the residues were dissolved in dilute acid, any copper present being separated as sulphide and estimated colorimetrically as copper pyridine thiocyanate (Spacu, *Bul. Soc. Stiinte Cluj*, 1922, **1**, 284). Only traces of copper were found, and these did not affect the tint of the permanganate.

			IV.	V.	VI.	
Mn salt taken	Nil.	Nil.	4·00	4·00	4·00	13·32
Cu salt taken (as mg. CuO)	3·12	3·12	3·12	3·12	3·12	1·04
Cu salt in filtrate (as mg. CuO)	0·03	0·01	0·08	0·08	0·06	0·03

When sodium hypochlorite is added to the double copper carbonate solution alone, the solution acquires a deep yellow colour, and gradually deposits a buff precipitate, which, on heating, is converted into a dense black precipitate. This behaviour emphasises another advantage of the use of the double copper carbonate in the reaction under study, *viz.*, the introduction of the copper into the reaction mixture in a form which is soluble and not readily precipitable. It was found that, if the copper had once become separated as a brown flocculent precipitate (*e.g.*, by the method described on p.1471, and in the presence of considerable alkali), the dense black precipitate phase did not occur, and the amount of permanganate formed was far from theoretical, nor could it be appreciably increased by further treatment of the residue. This is in agreement with the work of Müller (*Z. anorg. Chem.*, 1907, **54**, 417) on the formation of copper peroxide by the action of hypochlorite on copper oxide, who found that he could obtain the yellow peroxide only by the use of a clear blue alkaline *solution* of copper oxide. When a *suspension* of cupric hydroxide in alkali was used, he could not observe the formation of either the yellow copper peroxide or the black copper oxide phase.

When the method described above was applied to larger amounts of manganese (above 8 mg. MnO), the quantity of permanganate formed did not reach the theoretical value (XV—XIX).

	XV.	XVI.	XVII.	XVIII.	XIX.
Manganese taken	13·33	13·07	13·33	13·33	13·33
Permanganate formed	12·00	12·23	11·82	12·23	11·68

It was thought that this might be due to the premature decomposition of the buffer solution by loss of carbon dioxide before the comparatively large quantity of manganese had been converted to permanganate. To retard this loss as far as possible, the experiments were repeated, a stream of carbon dioxide being passed through the solution during the heating. At the end of 3 minutes' heating, and without check in the passage of the gas, a further 10 c.c. of sodium hypochlorite were added from a burette. After a further 2 minutes' heating the solution was filtered, and the permanganate estimated as before (XX—XXIII).

	XX.	XXI.	XXII.	XXIII.
Manganese taken	9·84	9·84	13·33	13·33
Permanganate formed	9·62	9·84	13·22	13·30

By this modified method practically all the manganese was converted to permanganate, as in the case in which smaller quantities of manganese were taken. Owing to the difficulty of estimating colorimetrically permanganate corresponding to more than 15 mg. of MnO, the method was not applied to amounts greater than this.

Reversibility of the Reaction.—When known amounts of permanganate were heated with approximately equivalent quantities of copper as double carbonate and with hypochlorite, no decrease in the amount of permanganate could be detected colorimetrically, and the precipitates, when tested by the bismuthate process, indicated only traces of manganese. It appears, then, that the reverse reaction is negligible in the case of copper, although when cobalt is substituted for copper an appreciable amount of permanganate is reduced.

Ratio of Manganese to Copper.—The most effective ratio of copper to manganese is not so well defined as is the case with other factors, and varies considerably according to the circumstances. For moderate amounts of manganese (1—5 mg. MnO), the presence of the equivalent quantity of copper leads to the best results, but with larger amounts of manganese the presence of approximately equivalent quantities of copper is not favourable to complete precipitation of the copper. Again, a large surface area of catalyst results in a relatively rapid decomposition of hypochlorite without perceptibly hastening the permanganate formation. This would have the effect of rendering the curve (Fig. 1) less steep, and delaying the attainment of the maximum value. With moderate amounts of manganese and very small quantities of copper, permanganate formation is incomplete, *e.g.*, 4·22 mg. MnO and 0·10 mg. CuO yielded permanganate equivalent to 3·70 mg. MnO. The precipitate was separated, washed, and heated with more hypochlorite, yielding a further 0·36 mg., and a third treatment of the precipitate gave 0·05 mg.

Increase in the ratio of cobalt to manganese shows a marked tendency to decrease the amount of permanganate formed.

Limit of Delicacy for Detection of Manganese.—The minimal quantity of manganese that could be detected by this method appeared to depend on the amount of permanganate capable of producing a visible tint : Manganese equivalent to 0·002 mg. MnO was converted to the theoretical amount of permanganate. For this purpose only 0·5 c.c. of sodium hypochlorite and 0·2 c.c. of sodium copper carbonate solution were used; a larger quantity of hypochlorite tended to mask the permanganate colour with a yellowish tint.

Mechanism of the Reaction.—It is evident that there is a pronounced difference between the functions of the copper oxide and of the cobalt oxide in this reaction :

(1) The hydroxyl-ion concentration, which is so critical a factor in the case of copper, appears to be comparatively unimportant in the case of cobalt, although large concentrations of alkali are prejudicial to permanganate formation.

(2) Other conditions being favourable, moderate amounts of manganese salts can be completely oxidised to permanganate in the presence of copper, independent of the amount of manganese present. When cobalt is used, however, the proportion of permanganate formed decreases in a regular manner with increasing amounts of manganese.

(3) The form and the mode of action of the precipitates of cobalt and copper differ in several respects. That of cobalt is flocculent, finely divided, and difficult to filter, and promotes copious evolution of oxygen from the hypochlorite throughout the reaction. The copper precipitate, at first flocculent, soon passes into a dense black residue, easily separated, and becomes considerably less active as regards hypochlorite decomposition after the formation of the permanganate has taken place.

(4) The cobalt, when used in the form of the double sodium carbonate, cannot be completely separated from the solution by boiling, as is the case with moderate quantities of copper.

It is suggested that the following probably represents the course of the main reaction, and is in agreement with the facts described in the foregoing pages. The first effect of the hypochlorite is to form copper peroxide and hydrated manganese dioxide. The oxidation of manganese dioxide to permanganate, which can proceed in the presence of manganese alone, is greatly accelerated by the copper peroxide, which gives up its active oxygen, possibly through the intermediate formation of an unstable compound of copper and manganese,* and is reconverted to the cupric form. At this stage

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* Some evidence for the existence of such an unstable intermediate compound is afforded by the following observations. If the manganese and copper salts are separately warmed with hypochlorite before mixing, and the combined solutions heated with a further quantity of hypochlorite, the amount of permanganate formed is much less than that obtained by the action of hypochlorite on the mixed salts.

much of the hypochlorite has been decomposed, and the hydroxyl-ion concentration, due to the alkali which is necessarily present in the hypochlorite solution, becomes an important factor. The excess of hydroxyl ions has an inhibitive effect on the formation of fresh copper peroxide, and the main reaction is arrested. If, however, the carbonate–bicarbonate mixture is used, (i) its buffer action renders the influence of the alkali negligible, and (ii) owing to the delayed precipitation of the copper, much of the earlier part of the reaction takes place in the liquid phase, and the oxidation of the manganese proceeds to completion.

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