was productive of very fine greenish bronze colored needles. Analysis of the crystals obtained in various ways show them to have the composition of the hydriodo-diiodide.

	Calc. for $(C_{11}H_{15}NO_2)_2.HI.I_2$:	Found:				
I_2	33.04	32.84	32.78	32.91	32.99	33.00
I_3	49.56	49.48	49.45	...	...	...
HI	16.65	16.64	16.67	...	...	...

Propiophenetidine Hydriodo-tetraiodide, $(C_{11}H_{15}NO_2)_2.HI.I_4$.—This compound was obtained in the form of fine purple-black silky needles by dissolving the preceding periodide, together with the calculated quantity of iodine, in a small volume of hot acetic acid and allowing the mixture to cool very slowly. After separation from the mother liquor in the usual way, the crystals melted air-dried and in a closed capillary at 92–4°.

	I_4	I_6	HI
Calc. for $(C_{11}H_{15}NO_2)_2.HI.I_4$	49.67	62.08	12.51
Found	49.72	62.35	12.63
	49.70	62.21	12.51

Both this and the diiodide are quite soluble in alcohol and acetic acid, only moderately so however in aqueous dilutions of these solvents.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE OTHO S. A. SPRAGUE MEMORIAL INSTITUTE LABORATORY OF CLINICAL RESEARCH, RUSH MEDICAL COLLEGE.]

THE ROLE OF ATMOSPHERIC OXYGEN IN THE OXIDATION OF GLUCOSE WITH POTASSIUM PERMANGANATE IN THE PRESENCE OF VARYING AMOUNTS OF ALKALI.

THE PRODUCTS OF OXIDATION.

BY EDGAR J. WITZEMANN.

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Although it has been known for many years that certain organic substances are capable of complete or partial oxidation in alkaline media through simple exposure to atmospheric air, the extent to which this process may participate in oxidations in alkaline media by means of permanganate, and presumably other oxidizing agents, has not been generally appreciated. The experiments here described show conclusively that maximum participation of atmospheric oxygen in permanganate oxidations occurs with concentrations of alkali corresponding approximately to 0.1 *N* potassium hydroxide. This participation diminishes with alkali concentrations greater or less than this amount. Thus in conducting oxidations with permanganate in the presence of alkali, for the purpose of measuring the quantity of oxidizable organic compound present on the basis of the permanganate consumed, it is as necessary to eliminate the participation of atmospheric oxygen as in any other quantitative oxidation method carried out in the presence of alkali; such for example as in any of the numerous sugar titration procedures.

The fact that this large participation of atmospheric oxygen occurs in oxidations with permanganate in alkaline solution was first noted in some earlier experiments on the complete oxidation of propylene glycol with potassium permanganate in alkaline solution[1]. It was found that at times as little as 80% of the calculated amount of permanganate was required for complete oxidation. The literature[2] indicated that the composition of the manganese oxide precipitate may be quite variable and contain much manganous oxide mixed with the dioxide. Thus it seemed possible that the extra oxidation could have been due to the reduction of the manganese dioxide to manganous oxide. But an analysis of the manganese oxide precipitate showed that the manganese is certainly all present as the dioxide in the alkaline oxidations. It was in this way that the extent of the participation of atmospheric oxygen in the oxidation was determined quantitatively.

Although numerous observations have already been made, which in a general way show that the character of the products obtained by the oxidation of certain organic substances in the presence of alkali (notably sugars) differ with varying concentrations of alkali, the present experiments show with precision the varying quantities of the sole end products (carbon dioxide and oxalic acid) which result from the complete oxidation of glucose by means of potassium permanganate for each initial concentration of alkali used (*i. e.*, between no alkali and 1.8 *N* KOH). It was also found that the relative quantities of carbon dioxide and oxalic acid formed not only vary with the initial concentration of alkali employed but also with the total quantity of alkali available, owing presumably to the fact that the initial alkali concentration falls as oxidation with its coincident acid formation progresses, except in those cases in which the total quantity of alkali added in proportion to the amount of glucose used was so excessive that such a fall in alkali concentration was almost negligible.

Experimental Part.

All the oxidations were carried out by dissolving 2 g. of pure crystalline *d*-glucose in 1000 cc. of water and adding variable amounts of potassium hydroxide as shown in the table. The oxidations were carried out in two series.

Series 1.—Expts. 1 to 8 were carried out by adding the amount of potassium hydroxide indicated in the table for each experiment before adding the permanganate. The permanganate was powdered and weighed (20 g. each) into small bottles, numbered to correspond with the solutions

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[1] Evans and Witzemann, THIS JOURNAL, 34, 1086 (1912).

[2] Cf. Gmelin-Kraut-Friedheim, *Hdb. der Anorg. Chem.*, 3, Part 2, p. 254 (1906–8), etc., for references.

to be oxidized. The oxidations were done at room temperature as follows: A small amount of the permanganate was added to each solution. The reaction in each case set in at a rate that was proportional to the concentration of the potassium hydroxide. This was especially true of Expts. 4, 5, 6 and 7. There were marked differences in the character of these precipitates. The difference was evident throughout the experiment and gave qualitative support to the idea that the variation in the amount of alkali causes marked differences in the physical character of the oxide of manganese formed in these reactions. Since Solutions 1, 2 and 3 did not become clear, *i. e.*, the manganese dioxide did not settle out, it was at first thought that oxidation was not taking place. Even after standing a month, or more, these red-brown solutions did not clear in the customary way. However, it was discovered that they could be further oxidized and the experiments were continued. As was learned later, these red-brown liquids were due to manganese dioxide in colloidal form.[1] Toward the end of the experiment these colloidal solutions were gradually precipitated as the concentration of the salts (mostly carbonates) increased.

After each addition of permanganate the mixture was agitated from time to time until the portion added was reduced. Permanganate was added in this way until the last portion was only reduced after standing several days and after frequent agitation. In a few cases in which an excess of permanganate had been added 1 cc. portions of 1% glucose solution were added from time to time, until reduction was complete. The unused permanganate in the original weighed portions was weighed and subtracted from the amount taken in the beginning. This gave in each case the amount of permanganate actually used (data given in Col. II in the table). Several weeks were required to complete the oxidations in this way.

Qualitative tests failed to reveal other products of oxidation than carbon dioxide and oxalic acid. Tests for acetic and formic acids and for substances reducing to Fehling's solution were negative in all experiments.

Series 2.—The second series (Expts. 9 to 15) of oxidations was carried out, in part, in order to verify the results of the first series and also in order to determine a little more accurately the conditions under which oxalic acid begins to be formed.

Analysis.

The total carbon dioxide in each experiment was determined by the method previously described[2] and the amount of carbon dioxide in the potassium hydroxide used was subtracted. This gave the total carbon dioxide formed in any experiment, plus any carbon dioxide that was absorbed from the air.

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[1] THIS JOURNAL, 37, 1079–91 (1915).

[2] *Loc. cit*

The oxalic acid in 50 cc. of the solution was precipitated as calcium oxalate in a boiling solution acid with acetic acid, by adding boiling calcium chloride solution. The precipitated oxalate was filtered off, washed, dissolved in sulfuric acid and titrated with potassium permanganate in the customary manner. In Expt. 13 a larger amount of the solution was required.

The analysis of the manganese dioxide precipitate offered certain difficulties. Owing to the fact that a considerable fraction of the precipitate is deposited as a mirror on the inside wall of the bottle and cannot be completely removed without dissolving it, an aliquot portion of the precipitate could not be used in the analysis. The following procedure gave little or no difficulty: After the analysis of the solution was complete or after sufficient for the analysis had been pipetted off[1] the precipitate was filtered off in a Büchner funnel in which a wet filter had been arranged so that the edge of the paper extended above the rim of the funnel. This large wet filter was thus folded into a rude filter cup, the wrinkled surfaces of which were pressed down to the surface of the Büchner. A filter of the proper size was previously placed in the funnel in order to support the paper filter cup. The precipitate was all transferred to the funnel and filtration and washing were carried out under suction. The bottle was frequently rinsed in order to wash out all oxalates, especially. The precipitate in the case of the strongly alkaline solutions was washed until it no longer gave a reaction to litmus. The other precipitates were likewise washed in the same way. The precipitate and filter papers were transferred to a large flask, 100 cc. of an oxalic acid solution (1 cc. equivalent to 0.05045 g. $KMnO_4$) were measured out carefully and part was added to the bottle and the remainder to the precipitate. Dilute sulfuric acid was added to both. The bottle was manipulated until all the manganese dioxide deposited on the glass was dissolved, and the contents were then added to the main portion. When all of the brown precipitate had been dissolved by warming (occasionally 20 cc. more of the oxalic acid solution had to be added) the solution was filtered, the filter washed and the filtrate diluted to one liter. An aliquot portion of the filtrate was titrated for oxalic acid in the usual way. For example, in Expt. 1, 100 cc. of the filtrate required 32.03 cc. of a potassium permanganate solution containing 0.002765 per cc., which corresponds to 0.8856 g. potassium permanganate for the entire filtrate. Therefore 5.045 g. (the potassium permanganate equivalent of the oxalic acid added) minus 0.8856 g. (the potassium permanganate equivalent of the oxalic acid not oxidized by the manganese dioxide) gives 4.16 g. as the potassium permanganate equivalent of the manganese dioxide sludge.

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[1] Under vacuum filtration these solutions frequently lose part of the carbon dioxide.

The individual data on the analytical determinations would not be of general interest and so will not be given. The final results in each case are given in the proper place in the table.

No.	I. G. glucose.	II. G. $KMnO_4$ used.	III. G. $KMnO_4$ calc.	IV. MnO_2 equiv. in g. $KMnO_4$.	V. MnO_2 equiv. calc.	VI. G. MnO_2 calc.	VII. $KMnO_4$ deficit from $KMnO_4$.	VIII. $KMnO_4$ deficit from MnO_2 equiv.	IX. Mols. KOH.
8	2.06	13.65	14.46	5.21	5.46	7.51	0.81 g.	0.25 g.	0
9	2.00	13.52	14.04	5.35	5.41	7.43	0.52	0.06	0
10	2.00	13.55	14.04	5.32	5.42	7.45	0.49	0.10	0
11	2.00	12.44	14.04	4.78	4.89	6.84	1.60	0.11	0.5
1	2.00	11.20	14.04	4.16	4.48	6.16	2.85	0.32	1.0
12	2.00	11.48	Expt. was lost		....	....	....	....	1.0
13	2.00	11.16	14.01	4.29	4.46	6.13	2.85	0.17	1.5
2	2.00	10.35	13.89	4.09	4.14	5.69	3.54	0.05	2.0
14	2.00	10.44	13.69	4.00	4.18	5.74	3.24	0.18	2.0
15	2.00	10.91	13.04	4.39	4.36	6.00	2.13	0	2.5
3	2.00	8.80	12.84	3.42	3.42	4.84	4.04	0	4.0
4	2.04	11.55	12.94	Lost		6.35	1.39	0	8.0
5	2.03	11.30	12.62	4.50	4.52	6.21	1.32	0.02	16.0
6	2.02	11.01	12.62	4.39	4.40	6.05	1.61	0.01	32.0
7	2.02	11.15	12.69	4.40	4.46	6.13	1.54	0.06	64.0

No.	X. G. KOH.	XI. *N* KOH.	XII. G. CO_2.	XIII. G. oxalic.	XIV. % CO_2.	XV. % oxalic.	XVI. % re-covered.	XVII. KOH for K_2 salts.	XVIII. KOH from $KMnO_4$.	XIX. Total KOH.	XX. KOH in ppt.
8	0	0	2.99	0	100	0	100	7.61	4.83	3.60	1.23
9	0	0	2.96	0	100	0	100	7.61	4.77	3.57	1.20
10	0	0	2.96	0	100	0	100	7.61	4.79	3.58	1.21
11	0.8	0.014	2.96	0	100	0	100	7.61	4.40	4.12	1.08
1	1.6	0.028	3.04	0	102	0	102	7.71	3.96	4.58	0.98
12	1.6	0.028	...	....	....	...	....	....	....	...	....
13	2.4	0.042	2.89	0.060	98.3	2.00	100.3	7.52	3.95	5.38	0.97
2	3.2	0.056	2.62	0.378	88.6	12.6	101.2	7.20	3.66	5.95	0.91
14	3.2	0.056	2.62	0.356	88.6	11.86	100.46	7.17	3.69	5.96	0.93
15	4.0	0.071	2.23	0.851	74.2	28.3	102.5	6.78	3.86	6.90	0.96
3	6.4	0.114	1.896	1.08	64.12	36.0	101.1	6.22	3.11	8.74	0.77
4	12.8	0.228	2.27	1.044	75.1	34.1	109.2	7.12	4.08	15.89	1.01
5	25.6	0.456	2.046	1.224	69.1	40.26	109.36	6.77	3.99	28.60	0.99
6	51.2	0.912	1.824	1.224	61.6	40.25	101.85	6.20	3.86	54.99	0.97
7	102.4	1.82	1.824	1.274	61.2	42.18	103.3	6.25	3.95	105.4	0.97

Discussion of the Results.

Quite a number of new observations were made in this series of experiments, which have little relation to each other. They will therefore be discussed without any special attempt to interrelate them.

Potassium Permanganate.—The immediate purpose of these experiments was to investigate the amount of potassium permanganate utilized in organic oxidations. The amount of permanganate necessary to completely oxidize the 2.00 g. of glucose in one liter of water in the presence of the amount of alkali given in Col. X is shown in Col. II. From the data on the sole products of oxidation, recorded in Cols. XII and XIII, the amount of permanganate that would theoretically be required to give these products was calculated as follows: To oxidize 2 g. $C_6H_{12}O_6$ to $3H_2C_2O_4$ requires 9 atoms of oxygen. If 2 molecules of $KMnO_4$ react in alkaline solution to give 3 atoms of oxygen it would require 10.52 g. $KMnO_4$ to oxidize the 2 g. of glucose completely to oxalic acid. In Expt. 13, 2% of oxalic acid was formed. Therefore 10.52 × 0.02 = 0.21 g., or the amount of $KMnO_4$ required to give this much oxalic acid. In oxidizing 2 g. of glucose completely to CO_2, 12 atoms of oxygen are required, and this corresponds to 14.04 g. $KMnO_4$. Since in Expt. 13 98.3% CO_2 were formed, 14.04 g. × 0.98.3 = 13.80 g. $KMnO_4$. 13.80 + 0.21 g. = 14.01 g. $KMnO_4$ or the total amount of $KMnO_4$ required to oxidize 2 g. glucose to the products obtained in Expt. 13. All of the others were calculated in the same way. The data are given in Col. III.[1]

By comparing the figures in Cols. II and III, it is seen that there is a deficit in the amount of permanganate actually utilized as compared with that calculated from the products of the reaction. It is also seen that this deficit increases as the alkali content is further increased. Thus the deficit previously observed in the oxidation of propylene glycol[2] was verified by the observations made in the case of glucose. In this case too the largest deficits occurred when alkali was present.

It might appear from these results therefore that oxidations with permanganate in alkaline solutions may result in the liberation of more than 3 equivalents of oxygen from one molecule of permanganate. In order to determine to what extent this hypothesis was tenable the amount of available oxygen in the manganese dioxide sludge in each experiment was determined. This was done in the manner described in the section on analytical methods.

The number of grams of permanganate to which the oxidizing power of the manganese dioxide sludge is equivalent is given in Col. IV. The calculated equivalents, obtained by multiplying the number of grams of permanganate used (Col. II) by $^2/_5$, are given in Col. V. The permanganate deficits as obtained by subtracting the values in Col. IV from those in Col. V are given in Col. VIII. These data do not in any wise tend to run parallel with the deficit obtained from the permanganate used as given in Col. VII. It has thus been definitely proved that the excess oxidation taking place in these solutions is not indicated by the final condition of the manganese dioxide precipitate.

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[1] It is naturally not assumed that a molecule of glucose is ever oxidized *in toto* to 3 molecules of oxalic acid. The calculation was made in this way solely for the sake of simplicity.

[2] *Loc. cit.*

If, however, the deficit given in Col. VIII is compared with the figures given in Col. XVII, which represent the total amount of potassium hydroxide necessary to convert all of the carbonic and oxalic acids present into their normal salts, and those in Col. XIX, which represents the total amount of alkali derivable from the hydrolysis of the permanganate used, plus the potassium hydroxide used, it is seen that the small deficit observed disappears almost completely when the total alkali present exceeds that necessary for the formation of normal salts. So that as far as these experiments go, there is no evidence for the idea that permanganate is reduced to manganous oxide in any but faintly alkaline solutions.

The observations in the case of neutral solutions are well supported by the exhaustive experiments of Smolka[1] on the oxidation of glucose in neutral solution, (*i. e.*, in the absence of alkalies), under a variety of conditions. These are apparently the only experiments in the literature in which the fate of the permanganate as well as that of the glucose has been followed quantitatively. Smolka oxidized 1 g. of glucose in boiling solution with potassium permanganate added in small portions until the solution remained permanently "red." 1 g. glucose required 6.920 g. $KMnO_4$ in order to be oxidized completely to carbon dioxide. For 2 g. glucose the $KMnO_4$ used would be 13.84 g., as compared with an average of 13.55 g. obtained in my own experiments carried out at room temperature. Smolka found 1.31% manganous oxide in his precipitate, which compares favorably with the average deficit of 2.5% observed in my own experiments conducted at room temperature. Smolka attempted to explain away both the permanganate deficit and the manganous oxide found as being largely due to experimental error. From my own experiments it would seem reasonable to expect that the experimental error would be about equal for the whole series. Since this obviously was not observed it must be concluded that there is actually some manganous oxide formed, but only in variable and small percentages when the oxidation is conducted in the manner described above.

The data in Col. VII show that the small deficit in the permanganate used increases rapidly when 0.5 molecule potassium hydroxide is present and apparently arrives at a maximum with 4 molecules of potassium hydroxide, or when the solution is 0.114 *N* alkali to begin with. From the figures in Cols. XVII and XIX it is seen that the solution must contain at least 2.52 g. free potassium hydroxide at the end of the experiment, *i. e.*, about 0.05 *N* alkali. With higher concentrations the deficit drops markedly. The fact that this effect is rather constant for similar conditions is shown by a comparison of the results of the two series, but especially by a comparison of Expts. 2 and 14. The unaccountable variations in

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[1] *Sitzungber. d. Math. Naturwissenschaftlichen Klasse d. Kais. Akad. Wissenschaften Wien.*, **95**, II, 5-30 (1887).

such experiments are illustrated by Expt. 15. In this case the permanganate deficit should have been more than 3 g. but was actually only 2.13 g. Smolka also found similar variations when using neutral solutions. These variations no doubt depend on slight but imperceptible variations in the technique.

There are three possible explanations of this permanganate deficit in alkaline solutions:

(1) A large proportion of the manganese dioxide is reduced to a manganous compound and subsequently oxidized by the air to manganese dioxide.

(2) The alkali serves as a catalyst in facilitating the oxidation of the glucose and the products of its reaction with alkali, by means of the oxygen of the air. The manganous compounds may have a role in this catalysis.

(3) The combined effect of (1) and (2).

There are no data in the literature that would entitle us to ascribe so large an effect to the first hypothesis.

On the contrary there is much evidence for the truth of the second hypothesis. The extensive work of Nef[1] and his pupils and others, on the incomplete oxidation of sugars and allied compounds, lends strong support to this hypothesis. Perhaps the most directly helpful experiments along this line are those of A. P. Mathews.[2] Sugar solutions containing various concentrations of alkali were placed in a closed system filled with oxygen. The diminution of oxygen pressure was measured on a manometer in the system. In this way sharp qualitative evidence of the marked effect of small alkali concentrations in producing a relatively enormous increase of the absorption of an oxygen atmosphere by sugar solutions was obtained. Accordingly, if arguments based on analogy in this way have any weight, this hypothesis seems the most probable.

It may be that the true explanation will involve both (1) and (2) as suggested in (3).

The elucidation of the mechanism of this excess oxidation will be of great theoretical interest, but in some ways the fact that it takes place at all, and more especially, the fact that it is so markedly induced by very small concentrations of alkali (even 0.014 N alkali gives a strong effect) and that it comes to a maximum at a low alkali concentration (about 0.1 N) is of greater practical interest.[3] In changing

[1] *Ann.*, **357**, 214 (1907); **376**, 1 (1910); **403**, 204 (1914).

[2] *J. Biol. Chem.*, **6**, 3–20 (1909).

[3] Mathews suggests that with glucose the maximum alkali effect was obtained at 0.2 N. According to my own experiments atmospheric oxidation was considerably less at 0.228 N than at 0.114 N, but this may be due in part to the fact that the addition of permanganate to Expts. 1, 2 and 3 was delayed at first, as stated above, owing to the fact that manganese dioxide was not precipitated at the beginning. On the other hand Mathews did not exclude the effect of the increasing solubility of oxygen in alkali solutions. The maximum, however, probably lies close to, or between, 0.1 or 0.2 N alkali. It is probable that the total available alkali is of great importance.

from no free alkali to a concentration of 0.114 N at the beginning and of 0.05 N at the end the maximum alkali effect has been obtained. The fact that minute concentrations of alkali influence many reactions very markedly has long been known, especially to the organic chemist, but such a relatively large and graded effect of small concentrations on organic oxidations, especially when such a powerful oxidizing agent as permanganate has been used, came as a surprise. The fact that this effect has been observed in three independent series of experiments on two different organic compounds (propylene glycol and glucose), and by Mathews working by another method, indicates clearly that these results are not anomalous. There are preliminary data already at hand which indicate that the alkali effect described is not found with all organic compounds and to a variable extent with others. If this proves true we now have a method of quantitatively studying these phenomena.

Products of the Oxidation.—The determination of the products of oxidation in this series of experiments was a secondary object. Smolka found that when glucose is completely oxidized with excess permanganate that the sole product is carbon dioxide. In one instance he found a trace of oxalic acid. In Expts. 8, 9 and 10 the calculated quantity of carbon dioxide was obtained, *i. e.*, 100%. In Expt. 11 0.5 molecule potassium hydroxide was used but the product was the same, likewise, in Expt. 1 in which one molecule of alkali was used. But in 13 with 1.5 molecules of alkali 0.60 g., or 2%, of oxalic acid was found. When the alkali was increased to 2 molecules, or 0.8 g. more alkali was used, the oxalic acid increased to 0.378 g. or 12.6%. The same result was obtained in number 14. From this point on the amount of oxalic acid increases, rapidly at first and then slowly to 1.274 g., or 42.18%, at 64 molecules of potassium hydroxide. Simultaneously there is always a corresponding fall in the carbon dioxide, so that the sum of the products in each case is equal[1] to 100% (cf. Cols. XII, XIII, XIV, XV, and XVII).

One of the most interesting facts brought out is the increase of the oxalic acid production from 2% to 12.6% on adding 0.8 g. additional potassium hydroxide. In seeking an explanation of this fact the calculations recorded in Cols. XVII, XVIII, XIX and XX were made. Col. XVII shows the number of grams of potassium hydroxide necessary to neutralize the carbon dioxide and oxalic acid to their normal salts. Col. XVIII shows the amount of potassium hydroxide that could arise from the permanganate, provided it is completely hydrolyzed. According to Morawski and Stingl[2]

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[1] The variations above 100% are due to the absorption of carbon dioxide from the air. In Expts. 4 and 5, in which the stoppers were subsequently found to have been defective, this error in the CO_2 rises to a maximum.

[2] *J. prakt. Chem.*, [2] **18**, 86 (1878); *Jahresber.*, **1878**, 275; cf. also Smolka, *Loc. cit.*, and Gmelin-Kraut-Friedheim. *Handbuch d. Anorg. Chem.*, **3**, II, 254, etc.

the precipitate in these experiments is $KH_8Mn_4O_{10}$ plus or minus small amounts of impurities. If we accept this statement as probably true in most of the experiments, the precipitate will contain part of the theoretically available alkali. The potassium hydroxide that could be used in this way was calculated from the data in Col. VI and is given in Col. XX. The figures in Col. XIX, which represent the amount of potassium hydroxide that should be available for neutralizing the carbonic and oxalic acids formed, are obtained by subtracting the values in Col. XX from the sum of those in X and XVIII.

From the figures in XVII and XIX it is seen that the alkali available becomes equal to the alkali required for normal salts in Expt. 15 and that under these conditions we get a maximum yield of oxalic acid. So that in this case the effect of the alkali in increasing the yield of oxalic acid is that it converts more and more of the acids formed into their normal salts and incidentally uses up the free alkali in the process. Now it happens that, of the dibasic aliphatic acids, oxalic acid is the only one known that is not attacked by permanganate in alkaline solution, so that as soon as enough alkali has been added to convert part of the oxalic acid into its normal salt that part becomes unavailable for oxidation if the conditions remain unchanged.

In oxidizing glucose with insufficient permanganate, Smolka found that one molecule of glucose gives one molecule of oxalic acid and four molecules of carbon dioxide, in the absence of alkali. When more permanganate was added the oxalic acid diminished until six molecules of carbon dioxide and no oxalic acid were obtained. The above experiments show that the latter conditions hold true when extra alkali is added, up to the point at which the amount of free alkali becomes equal to or in excess of that required to convert the products into their normal salts.

In calculating the percentage yield of oxalic acid it was assumed, in order to make the products recovered total 100%, that all the carbon is oxidized to oxalic acid, *i. e.*, three molecules of oxalic acid from each molecule of glucose. If, however, the above data of Smolka hold true in all cases, but one molecule of oxalic acid would be formed, *i. e.*, the maximum attainable yield would be 33% oxalic acid. The data show that this is not the true maximum. Furthermore, W. Greifenhagen, J. König, and A. Scholl[1] found on oxidizing various hexoses (0.20 g.), including glucose, in 40 cc. of boiling 20% potassium hydroxide with 50 cc. 0.1 *N* $KMnO_4$, that 2 molecules of oxalic acid and 2 molecules of carbon dioxide are formed, *i. e.*, 66% oxalic acid. Their quantitative data correspond very closely with this statement.

It is well known that glucose, as well as other sugars, undergoes marked changes in the presence of alkali and in the absence of oxygen, by which

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[1] *Biochem. Z.*, **35**, 168–93 (1911).

they are finally broken up into shorter chains which often rearrange, in part at least, into stable compounds such as lactic acid. Moreover, such shorter chain carbon derivatives tend to give quantitatively one molecule of oxalic acid and one of carbon dioxide with permanganate in strongly alkaline solutions.[1] So that although Greifenhagen, *et al.*, obtained about 66% of oxalic acid they were working under conditions in which the maximum decomposing effect of the alkali could be obtained, and therefore the maximum number of short chain molecules. In my own experiments, conducted at room temperature and with much smaller alkali concentrations, the decomposition of the glucose into molecules with shorter carbon chains would be relatively very much smaller. It is therefore clear that Smolka's formulation of the products of the oxidation holds only for the conditions under which he worked. As soon as excess alkali is present in the reaction solutions the signs of the decomposing action of the alkali would be preserved, since oxalic acid is stable under these conditions and since each shorter molecule tends to produce a molecule of oxalic acid. So that roughly, as far as we now know, the amount of oxalic acid in excess of 33% in these cases in which excess alkali was present may be taken as a measure of the amount of this decomposition.[2]

An additional bit of evidence for this interpretation was obtained thus: Expt. 3 was repeated. 2 g. glucose were dissolved in 1 liter of water and 6.40 g. potassium hydroxide were added to the colorless solution. The mixture was placed on the steam bath for $^3/_4$ hour and became rich brown in color and had an odor of caramel. After cooling it was treated with solid potassium permanganate a little at a time as usual. 8.52 g. potassium permanganate were required for complete oxidation. 1.255 g. oxalic acid were formed, or 41.83% of that theoretically possible if all the carbon in the glucose were converted into oxalic acid. Only 36% oxalic acid was obtained in Expt. 3. Thus it was shown that even warming a short time before oxidation markedly affects the yield of oxalic acid.

Resume.

It had previously been found in oxidizing propylene glycol with potassium permanganate in alkaline solution that only about three-fourths of the calculated amount of permanganate was utilized in some cases. A special series of experiments on the complete oxidation of glucose with permanganate, in the presence of variable amounts of alkali showed that this deficit in the amount of permanganate required occurs to a slight ex-

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[1] The three carbon compounds do not always, as was shown by Evans and Witzemann (*Loc. cit.*), quantitatively give one molecule of oxalic acid plus one molecule of carbon dioxide, in alkaline solution, but the statement is approximately true.

[2] Greifenhagen, *et al.*, have used a different interpretation which apparently holds true for the 6 carbon compounds but which breaks down with the 5, 4, 3 and 2 carbon compounds with which they also worked.

tent even in the absence of alkali, but increases rapidly on the addition of small amounts of alkali up to a concentration of about 0.1 *N*, after which it diminishes somewhat. By careful analyses of the manganese precipitate, it was found, in the solutions containing little or no alkali, that the oxidizing power of the precipitate was only slightly less than it would have been if all the permanganate used had been quantitatively converted into manganese dioxide. In the more alkaline experiments there was no deficit of this kind. It was thus shown that the excess oxidation in these experiments was not due to a permanent reduction of permanganate to manganous oxide. If it is thus reduced at first it was subsequently oxidized by atmospheric oxygen or permanganate to the peroxide. It is thought probable, however, that a considerable part of the permanganate deficit is due to the direct oxidation of the sugar in the alkaline solution by atmospheric oxygen. Both of the preceding processes may, however, play a part in producing the permanganate deficit. But, whatever the mechanism of this excess oxidation may be, it was clearly demonstrated that the excess oxidation was due to the action of atmospheric oxygen in some way.

The sole products of the complete oxidation of glucose under these conditions are carbon dioxide and oxalic acid. It was shown that the oxalic acid increases very rapidly from none to a large amount within small range of change in alkalinity. But it was successfully proved from the data that this is not solely a question of the initial concentration of the alkali, but is also dependent on the degree to which the initial concentration is maintained. Oxalic acid or potassium acid oxalate are not stable in permanganate solution, so that such oxalic acid as is formed cannot persist even in part until the amount of alkali present is sufficient to convert it into normal potassium oxalate (which is stable in permanganate solution).

Some deductions about the mechanism of the formation of oxalic acid were also made.

CHICAGO, ILL.

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