426. *Studies in Electrolytic Oxidation. Part II. Further Experiments on the Electrolytic Oxidation of Sodium Thiosulphate.*

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In Part I (this vol., p. 2345) the electrolytic oxidation of sodium thiosulphate at a smooth platinum electrode was described, and a mechanism involving the primary formation at the anode of hydrogen peroxide as the effective oxidising agent was proposed. In the ordinary oxidation of thiosulphate by hydrogen peroxide, two alternative reactions, one leading to the formation of tetrathionate and the other to sulphate, are possible; normally the former reaction is favoured, but Abel and Baum (*Monatsh.*, 1913, **34**, 425) found that in dilute acetic acid solution small quantities of molybdic acid markedly increased the proportion of sulphate formed. This fact appears to provide a specific test for the truth of the hydrogen peroxide theory of electrolytic oxidation. Experiments have now been made on the influence of small quantities of ammonium molybdate on the products of the anodic oxidation of thiosulphate in acid (p_H 5) solution; although the results were at first negative, the conditions were eventually discovered under which 34% of the thiosulphate was oxidised to sulphate in the presence of molybdate, whereas only 1% was so oxidised in its absence. The theory proposed appears thus to be strikingly confirmed.

The oxidation of thiosulphate has also been studied at a stationary smooth platinum electrode, and at rotating electrodes of platinised platinum, nickel, gold, and carbon. The results are definitely opposed to the conversion of thiosulphate into tetrathionate being a direct electrical process, but are in harmony with the view that a secondary chemical reaction occurs in which hydrogen peroxide is the oxidising agent.

EXPERIMENTAL.

The exptl. method was identical with that described in Part I (*loc. cit.*); the platinised Pt, Au, and Ni electrodes were made by the electrodeposition of the appropriate metal on a Pt base, which was almost identical in size and construction with the smooth Pt anode used in the experiments described in Part I and in portions of the present work. The C anode consisted of a rectangular plate of gas C having an apparent area of 15 sq. cm. Unless otherwise stated, the electrodes were rotated at a speed of approx. 550 r.p.m.

Influence of Molybdic Acid.—A 0·025*M*-$Na_2S_2O_3$ solution in p_H 5 acetate buffer was made 0·01*M* with respect to $(NH_4)_2MoO_4$ and electrolysed with the smooth Pt anode at various currents from 0·05 to 0·001 amp. No appreciable increase in the amount of SO_4'' above the normal value could be detected. Examination of the observations of Abel and Baum (*loc. cit.*) accounts for this negative result. The velocity of the reaction between H_2O_2 and S_2O_3'' which leads to S_4O_6'' formation is directly dependent on the H_2O_2 concn., whereas the rate of that resulting in SO_4'' in the presence of molybdic acid is independent of this concn. Abel and Baum worked with dil. solutions of H_2O_2, but at an anode the H_2O_2 will probably be formed in a layer of high local concn., and under these conditions tetrathionate formation may become much faster than the alternative sulphate reaction even in the presence of large amounts of molybdate. In order to make appreciable, therefore, the relative increase in the yield of sulphate, it is necessary to choose the conditions so that the concn. of H_2O_2 at the anode is greatly diminished; this can most readily be attained by the addition of a catalyst for the decomp. of H_2O_2. Bredig and Müller von Berneck (*Z. physikal. Chem.*, 1899, **31**, 277) observed that the catalytic activity of $MnSO_4$ for the decomp. of H_2O_2 was decreased in acid solution, although it is still an effective catalyst (Tatu, *Tiba*, 1931, **9**, 473; see *A.*, 1932, 128), and it has been found in the present work that in the anodic oxidation of 0·025*M*-$Na_2S_2O_3$ in an acetate buffer of p_H 5, the addition of 0·001*M*-$MnSO_4$ reduces the oxidation efficiency from 90% to about 50%. This solution (0·025*M*-$Na_2S_2O_3$, 0·001*M*-$MnSO_4$, p_H 5) was used to determine the influence of the addition of molybdate. In order to make the results of the experiments comparable, sufficient electricity was passed through the solutions to ensure almost complete oxidation of the thiosulphate in each case, allowance being made for the low yields due to catalytic decomp. of the H_2O_2 and to the formation of SO_4''; with a current of 0·05 amp. the following results were obtained:

Influence of Molybdate on the Oxidation of 0·025*M*-$Na_2S_2O_3$ *in the Presence of* $MnSO_4$ *at* p_H 5.

	S_2O_3'' oxidised, %.	S_2O_3'' converted into S_4O_6'', %.	S_2O_3'' converted into SO_4'', % (by diff.).
Without molybdate	95	94	1
With 0·01*M*-$(NH_4)_2MoO_4$ ...	95	61	34

The relative amounts of SO_4'' formed were approx. checked by pptn. as $BaSO_4$. The results confirm the view that H_2O_2 is the effective agent in the anodic oxidation of $Na_2S_2O_3$.

Stationary Platinum Electrode.—A 0·025*M*-$Na_2S_2O_3$ solution in phosphate buffer of p_H 7 was electrolysed with a current of 0·01 amp., the Pt electrode being rotated in the normal manner; the expt. was then repeated with the electrode stationary. The results are given below : Q_b (see Part I, p. 2348) refers to the number of coulombs passed before the sudden increase of potential occurred.

	Q_b.	S_2O_3'' oxidised, %.	S_2O_3'' converted into S_4O_6'', %.
Rotating anode	100	90	79
Stationary anode	21	53	40

If the electrode reaction involved the direct electrical discharge of S_2O_3'' ions, almost identical values would have been anticipated for stationary and rotating electrodes, since the only factor likely to affect the results is diffusion, and the current used was much below that at which diffusion effects become appreciable. On the basis of the H_2O_2 theory, however, it may be supposed that at a stationary electrode there will be a higher local concn. of H_2O_2 than at a rotating one; the rate of spontaneous decomp. will therefore be greater and consequently the oxidation yields will be lower and polarisation, as indicated by the low value of Q_b, more rapid. This is in agreement with the actual observations.

Platinised Platinum Electrode.—Prior to use, the anode was cleaned, but not heated, and its O content controlled in the usual manner (Part I, p. 2347). The results obtained under various conditions for the passage through 0·025*M*-$Na_2S_2O_3$ of the quantity of electricity (at 0·05 amp.) required theoretically to bring about complete oxidation (241 coulombs) are given in Table I (cols. *a*).

TABLE I.

Current Efficiency for the Oxidation of 0·025*M*-$Na_2S_2O_3$ *at* (a) *Platinised Platinum and* (b) *Gold Anodes.*

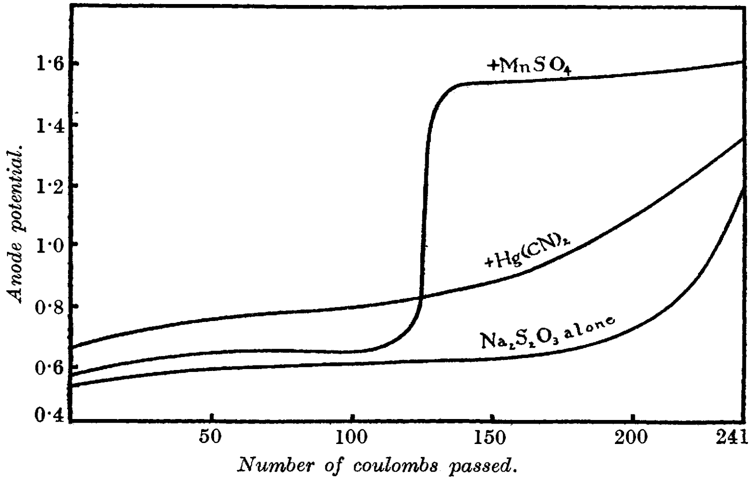
	S_2O_3'' oxidised, %.		S_2O_3'' converted into S_4O_6'', %.	
	(*a*)	(*b*)	(*a*)	(*b*)
p_H 5	89	22	89	18
7	93	71	91	65
9	52	51	47	42
p_H 7 { +$Hg(CN)_2$ 0·001*M*	84	—	76	—
p_H 7 { +$MnSO_4$ 0·001*M*	51	0	46	0
p_H 7 { +$CoSO_4$ 0·001*M*	61	30	56	28

The effects of the p_H of the electrolyte on the current efficiency and on the formation of tetrathionate are similar to those with a smooth Pt anode, except that the effect of alkalinity in reducing the yield is here more marked; the slight decrease in the weakly acid solution does not appear to have any special significance. The addition of $Hg(CN)_2$ produces a small but definite diminution in the current efficiency, whereas at a smooth Pt anode no such decrease was observed. In the presence of platinised Pt as catalyst, O gas is able to oxidise S_2O_3'' slowly to S_4O_6'', and part of the normal yield in the electrolytic oxidation at an anode of this material is probably due to free O resulting from the decomp. of H_2O_2; $Hg(CN)_2$ appears to be able to poison the Pt for the oxidation with O and so reduces the anodic oxidation efficiency. The results in the presence of $Hg(CN)_2$ may thus be regarded as the true *electrolytic* oxidation efficiency at a platinised Pt electrode.

The results with catalysts for H_2O_2 decomp. are as expected; the decreased effects, as compared with smooth Pt, are due to (1) the greatly increased area of the anode and the consequent lower superficial concn. of catalyst, and (2) oxidation brought about by the liberated O gas. It is noteworthy that $MnSO_4$ does not inhibit the oxidation of S_2O_3'' by gaseous O in the presence of platinised Pt; experiments made in the course of the present work indicate, in fact, that it may to some extent promote the reaction.

The potential–time curves for 3 expts., at p_H 7, are shown in Fig. 1. The increased area of the anode and the utilisation of the liberated O for oxidation tend to delay the rise to the higher potential stage; the addition of $Hg(CN)_2$ or of $MnSO_4$ results in an earlier increase of potential, the former by poisoning the electrode for a particular type of O adsorption, and the latter by increasing the rate of O accumulation.

Fig. 1.



Gold Electrode.—Before use in electrolysis, the electrode was treated in the usual manner except that it was not heated to redness. The results obtained after the passage of 241 coulombs of electricity at 0·05 amp. through 0·025M-$Na_2S_2O_3$ are in Table I (cols. *b*); the figures are not as reproducible as those obtained with the Pt electrode, probably on account of the slight tendency to dissolution shown by a Au anode in S_2O_3'' solution. The results, apart from those for the p_H 5 solution, are in excellent agreement with the theory of electrolytic oxidation of S_2O_3'' by H_2O_2. The current efficiency in the slightly acid solution is, however, unexpectedly low and requires explanation. It was noted that during the course of the electrolysis the anode was attacked, particularly in the more acid solution, and Au was detected in the electrolyte; it appeared possible that the low oxidation efficiency at p_H 5 might be accounted for by an inhibiting effect of the dissolved Au on the oxidation of S_2O_3'', the mechanism probably being the catalytic decomp. of the H_2O_2. This possibility was tested as follows: quantities of $Na_3Au(S_2O_3)_2,2H_2O$, sufficient in amount to make the solutions approx. $0{\cdot}005M$ with respect to Au, were dissolved in $0{\cdot}025M$-$Na_2S_2O_3$ in p_H 5 and p_H 7 buffers; the total S_2O_3'' in each solution was then estimated and found to be $0{\cdot}037M$. These solutions were electrolysed at 0·05 amp., a smooth Pt anode being used, and analysed after the passage of the theor. quantity of electricity; the results are compared below with those obtained when the Au compound was absent.

Influence of Dissolved Gold on the Current Efficiency for the Oxidation of S_2O_3'' *at a Platinum Anode.*

	S_2O_3'' oxidised, %.		
	Without Au.	With Au.	Decrease.
p_H 5	90	65	25
7	85	71	14

There is little doubt that when Au is dissolved in a S_2O_3'' solution it is able to inhibit to some extent the anodic oxidation, particularly at p_H 5. When it is remembered that in the course of the dissolution of the Au anode the inhibiting agent is formed at the place where it can be most effective, the abnormally low oxidation efficiency of S_2O_3'' with an anode of Au at p_H 5 may be readily accounted for.

The potential of the Au anode in the p_H 7 solution varied in a curious manner during the electrolysis; starting at about 1·25 volts (on the H scale) it tended first to rise, but after a time fell below its initial value (to 1·21 volts) and then commenced to rise steadily during the remainder of the electrolysis, reaching 1·48 volts at the conclusion. In the p_H 9 solution and in the presence of catalysts for the decomp. of H_2O_2, the rise of potential was continuous from the commencement. Two opposing factors appear to be operative at the Au anode, *viz.*, the accumulation of O, tending to raise the potential, and the dissolution of the surface oxide by S_2O_3'' solution, tending to delay polarisation; the potential of the electrode will rise or fall according as one or the other factor predominates. In the p_H 5 solution of S_2O_3'' a regular periodic fluctuation of potential was observed during electrolysis with an electrode which had been cleaned with HCl before use.

Nickel and Gas-carbon Electrodes.—The Ni anode was cleaned with dil. HCl and its O content controlled in the usual manner before use. The C anode was cleaned with boiling H_2O and used directly without further treatment. The results of the electrolyses of $0{\cdot}025M$-$Na_2S_2O_3$ at 0·05 amp. are given in Table II.

TABLE II.

Current Efficiencies for the Oxidation of $0{\cdot}025M$-$Na_2S_2O_3$ *at* (a) *Nickel,* (b) *Carbon Anodes.*

		S_2O_3'' oxidised, %.		S_2O_3'' converted into S_4O_6'', %.	
		(*a*)	(*b*)	(*a*)	(*b*)
p_H 5		80	58	78	54
7		67	57	60	51
9		38	34	28	26
p_H 7	$+MnSO_4$ $0{\cdot}001M$	0	7	0	6
	$+CoSO_4$ $0{\cdot}001M$	31	36	28	25

The results for a Ni anode are in agreement with those obtained at Pt and require no comment. The anode potential in the p_H 7 solution remained almost constant at 1·34 volts during the greater part of the electrolysis; in the presence of $MnSO_4$ and $CoSO_4$ the potential was raised. In the p_H 5 solution, and even at p_H 7 when small currents were used, there were definite indications of a lower-potential stage, such as that observed with smooth Pt (see Part I), at 0·9—1·1 volts, followed by a sudden rise to the higher-potential stage (1·35 volts). It was not possible, however, to obtain reproducible results, probably because of the difficulty of obtaining a const. initial O content of the anode.

At the C anode the slightly higher efficiencies for the oxidation in the presence of $MnSO_4$ and $CoSO_4$, as compared with the results for smooth Pt, Au, and Ni anodes, may be accounted for by the larger specific area of the electrode and the consequent lower superficial concn. of the catalyst for the decomp. of H_2O_2. The anode potential of the C electrode remained fairly steady at about 1·35 volts during the course of the oxidation of S_2O_3'' at p_H 7.

DISCUSSION.

A review of the results obtained in the present work with platinised platinum, gold, nickel, and gas-carbon anodes shows that increase of p_H of the electrolyte brings about a decrease in the current efficiency for the oxidation of thiosulphate, but at the same time there is an increase in the ratio of sulphate to tetrathionate formed. The only apparent exception to this generalisation is the low efficiency obtained at p_H 5 with a gold anode; in this case there is little doubt, as shown in the experimental portion, that the gold which is dissolved from the anode inhibits the oxidation of the thiosulphate, and so the low yield is readily explained. All the observations on the influence of p_H, as well as those on the effect of the addition of manganous or cobaltous sulphate to the electrolyte, are in excellent agreement with the theory already proposed (Part I) that hydrogen peroxide is the effective agent in the anodic oxidation of thiosulphate. The experiments with molybdate appear to supply definite confirmation of this view.

It should be possible to correlate the oxidation efficiencies at various anodes with the catalytic effects of these materials on the decomposition of hydrogen peroxide; if the substance is a good catalyst for this decomposition, the efficiency of oxidation of thiosulphate should be low. The following values indicate the amounts of thiosulphate oxidised in a p_H 7 solution with a current of 0·05 amp.: Pt 85, platinised Pt 84, Au 71, Ni 67, gas C 57%. (The figure for platinised Pt is that obtained in the presence of mercuric cyanide, see p. 2802). According to the theory proposed, therefore, the catalytic effect on the decomposition of hydrogen peroxide should increase for the various substances in the order given. It is difficult to obtain direct information concerning the catalytic influences of these materials under the conditions of the present experiments, but some general conclusions may be drawn from the results of other observers. Platinum in a finely divided state is a good catalyst for the decomposition of hydrogen peroxide, but it was shown by Bredig and Ikeda (*Z. physikal. Chem.*, 1901, **37**, 62) that its activity is almost completely inhibited by the poisoning effect of thiosulphate ions; further, a similar inhibition appears to be brought about by anodic polarisation (Spitalsky and Kagan, *Ber.*, 1926, **59**, 2900). Under the conditions of electrolysis, therefore, platinum should be a poor catalyst for the peroxide decomposition, and should give a high efficiency for the oxidation of thiosulphate. Platinised platinum, with its greater surface, may be expected to be a better catalyst and so will give lower yields than smooth platinum; although the observed difference is not marked, it must be remembered that the actual current density at the platinised electrode is much less than at the smooth anode and low currents tend to give an increased oxidation efficiency (Part I, p. 2348). Finely divided gold is a good catalyst for the decomposition of hydrogen peroxide and is only slightly poisoned by thiosulphate ions (Bredig and Reinders, *Z. physikal. Chem.*, 1901, **37**, 338); the oxidation efficiency at a gold anode might thus be expected to be lower than at platinum. There is little definite information available concerning the catalytic influences of nickel (or its oxide) and gas carbon; Thénard ("Traité de Chimie," 1827, Vol. II, pp. 70, 72, 76) records nickel (and its oxide) as being moderate catalysts and charcoal as a good catalyst. If these substances are not readily poisoned by thiosulphate, their respective effects on its anodic oxidation may be correlated with their influence on the decomposition of hydrogen peroxide.

If the electrolytic oxidation of thiosulphate to tetrathionate involved the reversible discharge of S_2O_3'' anions the electrode potential should be almost independent of the nature of the anode material. The fact that the potentials at the gold, nickel, and gas-carbon electrodes used in the course of the present work were in the vicinity of 1·3—1·4 volts during the major portion of the electrolysis might indicate that such a reversible discharge occurs at these anodes; it must be remembered, however, that at a platinised platinum anode the potential is in the vicinity of 0·5—0·7 volt, whereas at smooth platinum oxidation may occur completely at 0·8 volt or at 1·5 volts according to the current used. There is every reason to believe, from the effects of p_H and of catalysts, that the reaction mechanism is the same at all the electrodes studied, and so the similarity of the anode potentials at gold, nickel, and carbon must be regarded as fortuitous.

SUMMARY.

1. The yield of sulphate obtained in the electrolytic oxidation of thiosulphate ions under suitable conditions may be increased by the

presence of molybdic acid; a similar increase is brought about by molybdic acid when thiosulphate is oxidised by hydrogen peroxide.

2. A study has been made of the oxidation of thiosulphate ions in well-buffered solutions at platinised platinum, gold, nickel, and gas-carbon anodes. In general, an increase of p_H results in a decrease of the current efficiency for oxidation, but there is an increase in the ratio of sulphate to tetrathionate formed.

3. The presence of manganous or cobaltous sulphate, which are catalysts for the decomposition of hydrogen peroxide, brings about a marked reduction of oxidation efficiency at all the electrodes studied.

4. The results are in harmony with the view that anodic oxidation of thiosulphate is a secondary chemical process in which hydrogen peroxide is the effective oxidising agent.

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