THE ELECTROLYTIC PREPARATION OF HYDROGEN PEROXIDE

Part I. The Intermediate Production of Sodium Persulphate

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THE present investigation arose out of the work of Joshi, Solanki and Sheshadri[1] who have worked out the optimum conditions for the electro-chemical preparation of hydrogen peroxide from sulphuric acid. Though simple, this method is subject to limitations owing to the fact that the current yield of the intermediately formed perdisulphuric acid, ($H_2S_2O_8$), is affected by its comparative instability under ordinary conditions. It was of interest, therefore, to investigate the utilisability of aqueous sodium sulphate as a starting material instead of sulphuric acid, so that the intermediate product is the stabler sodium salt of perdisulphuric acid. This on distillation under appropriate conditions yields hydrogen peroxide. The preparation of hydrogen peroxide in this way may be divided into two main parts: (i) the electro-chemical preparation of sodium persulphate and (ii) the distillation, concentration and stabilisation of hydrogen peroxide from sodium persulphate.

A review of the literature having shown that no detailed information is available for the preparation of sodium perdisulphate except in a German Patent,[2] an investigation in some detail has been carried out on the optimum conditions for its electro-chemical preparation.

EXPERIMENTAL

The cell consisted of a glass jar 12″ × 4″ fitted with a perforated stopper carrying a pair of platinum electrodes, a thermometer and an exit tube for the evolved gases. The electrolytic cell was cooled by immersion in a well stirred freezing mixture so that a temperature of 5 to 10° C. as desired was maintained during electrolysis. 50 c.c. of aqueous sodium sulphate of known concentration formed the bath solution, except in Expts. reported in Table IX. The circuit included an ammeter, an adjustable resista n and a voltmeter between the two electrodes. After the cessation of electrolysis, 5 c.c. of the electrolyte was analysed for the total active oxygen, by treatment with an excess of standard $FeSO_4$ solution in an inert atmosphere; the excess of the $FeSO_4$, was then determined by back-titration with N/20 $KMnO_4$. From this, and the quantity of electricity passed through the electrolyte the current efficiency, C.E. is calculated from Faraday's Law. The following is a typical calculation from Expt. 1 in Table VIII.

Blank-titre for 10 c.c. $FeSO_4$ .. .. — 21·1 c.c. N/20 $KMnO_4$
Back-titre after treatment with 5 c.c. of electrolyte .. .. 5·4 c.c. ,, ,,
Active oxygen in 5. c.c of the electrolyte .. — 15·7 c.c. ,, ,,
Total active oxygen in 50 c.c. .. .. —157·0 c.c. ,, ,,
Quantity of electricity passed .. .. —0·25 amp. hr.

Corresponding to 100% C.E., the current efficiency, 26·86 amp. hrs. of electricity should produce active oxygen equivalent to 1,000 c.c. of N. $KMnO_4$.

The C.E. in the above case .. .. $\frac{157 \times 26\cdot86 \times 100}{0\cdot25 \times 20 \times 1000}$
84·0%

The C.E. has been studied in respect of the following factors: Conc. $Na_2SO_4.10H_2O$ in neutral solution (Table I); conc. $Na_2SO_4.10H_2O$ in dil. sulphuric acid (Table II); conc. sulphuric acid (Table III); anodic and cathodic current densities (Tables IV and V); inter-electrode distance (Table VI); temperature (Table VII); duration of electrolysis (Table VIII); current concentration (Table IX); addition agents (Table X) and the use of a diaphragm.

TABLE I

Influence of the Concentration of Na_2SO_4, $10H_2O$ on C.E.

Anodic current density .. 55·2 amps./dm^2
Cathodic current density .. 15·0
Temperature .. 10°C
Duration of electrolysis .. 30 mins.
Current .. 1 amp.
Inter-electrode distance .. 1·5 cm.

Conc. Na_2SO_4, $10H_2O$ (gms./100 c.c.)	P. D. (Volts)	Total active O_2 (c.c N/20 $KMnO_4$)	C. E. %
10	4·5	2	0·5
20	do	4	1·1
30	do	3·5	0·9
40	do	4	1·1

TABLE II

Influence of the concentration of Na_2SO_4, $10H_2O$ in 4N H_2SO_4 on C.E.

Conditions same as in Table I.

Conc. Na_2SO_4, $10H_2O$ (gms./100 c.c.)	P. D. (Volts)	Total active O_2 (c.c N/20 $KMnO_4$)	C. E. %
15	4·8	155	41·6
25	do	175	47·0
45	do	203	54·5

TABLE III

Influence of Concentration of H_2SO_4 on C.E.

Conc. of Na_2So_4, 10 H_20 — 40 gms./100 c.c.
Other conditions same as in Table II.

Conc. H_2SO_4 (gms./100 c.c.)	P. D. (Volts)	Total active O_2 (c.c N/20 $KMnO_4$)	C. E. %
5	4·5	44·1	11·6
10	4·5	74·0	19·5
20	4·6	111·0	29·2
30	4·6	157·0	41·3
40	4·7	217·0	57·1
50	4·8	235·0	62·1
60	4·8	277·0	73·1

TABLE IV

Influence of Anodic Current Density on C.E.

Composition of both solution | 40 gms. of Na_2 So_4, $10H_2O$ &
60 gms. of H_2 So_4/100 c.c.

Current varied as indicated in 1st column.
Other conditions same as in Table III.

Current (amps)	Anodic C. D. (Amps./dm^2)	P. D. (Volts)	Toral active O_2 (cc N/20 $KMnO_4$	C. E. %
0·3	16·6	3·6	59	59·9
0·5	27·6	3·8	118	62·7
1·0	55·2	5·1	272	71·7
1·5	82·8	5·8	407	71·5
2·0	110·3	6·8	531	70·0
3·0	165·5	8·5	765	67·2

TABLE V

Influence of Cathodic Current Density on C.E.

Anodic C. D. — 55·1 amps./dm²
Current 1 1 amp.
Other conditions same as in Table IV.

Cathodic C. D. (amps./dm²)	P. D. (Volts)	Total active O_2 (c.c N/20 $KMnO_4$)	C. E. %
15·0	4·7	243	64·1
18·5	5·5	235	61·9
82·6	6·0	225	59·2

TABLE VI

Influence of Inter-Electrode Distance on C.E.

Cathodic C. D. — 15·0 amps./dm²
Other conditions same as in Table V.

Inter-Electrode distance (cm.)	P. D. (Volts)	Total active O_2 (c.c N/20 $KMnO_4$)	C. E. %
1·5	4·4	240	63·3
2·3	4·6	239	63·0
3·5	4·8	238	62·7
4·0	5·0	234	61·7

TABLE VII

Influence of Temperature on C.E.

Inter-Electrode distance — 3·4 cm.
Other conditions same as in Table VI.

Temperature (°C)	P. W. (Volts)	Total active O_2 (c.c N/20 $KMnO_4$)	C. E. %
5	5·8	228	60·0
10	5·0	242	63·8
15	4·8	240	63·3
20	4·7	233	61·4
30	4·3	195	51·2
40	4·0	129	33·9
50	3·8	83	21·9

TABLE VIII

Influence of Duration of Electrolysis on C.E.

Temperature — 10°C.
Other conditions same as in Table VII.

Time (mins.)	P. D. (Volts)	Total active O_2 (c.c N/20 $KMnO_4$)	C. E. %
15	4·8	157	84·0
30	4·8	240	63·3
45	4·9	326	58·5
60	5·0	408	54·7
90	4·9	577	51·6
120	4·8	731	49·0
240	4·3	1379	46·3

TABLE IX

Influence of Current Concentration on C.E.

Duration — 30 mins.
Volume of electrolyte varied as indicated.
Other conditions same as in Table VIII.

Vol. of electrolyte (c.c.)	Current conc. (amps./100 c.c)	P. D. (Volts.)	Total active O_2 (c.c N520 $KMnO_4$)	C. E. %
100	1·5	4·5	257	68·8
75	1·4	4·5	256	68·5
50	2·8	4·8	249	66·6

TABLE X

Influence of Addition Agents on C.E.

Temperature — 10°C.
Composition of bath solution | 40 gms. Na_2 So_4, 10 H_2O
60 gms. H_2 So_4 and
1 gm. addition agent per 100 cc. solution

Other conditions same as in Table VIII.

Addition agent	P. D. (Volts)	Total active O_2 (c.c N/20 $KMnO_4$)	C. E. %
$K_2Cr_2O_7$ ..	4·7	168	45·1
$Pb\ (CH_3CO_2)_2$ ..	4·6	186	50·0
$MnSO_4 \cdot 7H_2O$ ..	4·8	195	52·4
Al_2O_3 ..	4·7	202	54·3
$MgSO_4 \cdot 7H_2O$ ..	4·6	216	58·0
$Fe_2(SO_4)_3$ ..	4·8	223	59·9
CeO_2 ..	4·7	227	61·0
$CoSO_4 \cdot 7H_2O$ ..	4·6	240	64·5
HCl ..	4·8	241	64·7
Na_2HPO_4 ..	4·7	250	67·1
$NiSO_4 \cdot 7H_2O$ ..	4·7	273	73·3
$KClO_4$ ..	4·6	276	74·1
HF ..	4·6	303	81·4

DISCUSSION

When a neutral aqueous solution of sodium sulphate is electrolysed between platinum electrodes, the hydrogen and oxygen evolved are in the ratio 2 : 1 to a good approximation. The characteristic smell of ozone, however, can be observed clearly even at 5° C. for the bath temperature. The net result of electrolysis is apparently the decomposition of water into its elements. When, however, the solution of sodium sulphate is acidified with sulphuric acid, it is observed that the evolution of oxygen at the anode is considerably lower; the actual volume of the oxygen liberated is less than half of the cathodic hydrogen. This diminution in the amount of oxygen is associated with the acquirement of strong oxidising properties by the electrolyte. It is due to the formation of perdisulphuric or Marshall's acid ($H_2S_2O_8$) at the anode, which depends on the concentration of sodium sulphate and sulphuric acid on the bath (*cf.*, Tables II and III).

Various theories exist in literature regarding the electrolytic formation of perdisulphuric acid and its salts at the anode. According to a well-worked out theory due to Richarz[3] perdisulphuric acid is formed at the anode by the polymerisation of discharged HSO_4'-ion pairs, according to the equation

$$2HSO_4' = H_2S_2O_8 + 2 - \qquad (1)$$

It follows from (1) that the precedent condition necessary for the formation of perdisulphuric acid is a sufficient concentration of the HSO_4'-ions in the bath. The rate of the polymerisation of the discharged HSO_4'-ions would also be a determining factor. These deductions are in agreement with the general experimental results.

It must be pointed out, however, that though the above theory explains the formation of perdisulphuric acid and its potassium and sodium salts, it fails almost completely to account for the high current yields obtained in the electrolysis of a neutral solution of ammonium sulphate, in which there are practically few HSO_4'-ions. This has been explained by assuming the polymerisation of SO_4''-ions according to the equation

$$2SO_4'' = S_2O_8'' + 2 - \qquad (2)$$

It may be suggested that the anomaly shown by ammonium sulphate may be due to the well-known peculiar structure of the ammonium ion, which has been found to show a different electro-chemical behaviour from that of the other cations.

Another theory which has been put forward by Foerster[5] and may be considered as an improvement on the view of Traube[6] that the perdisulphuric acid is produced by the oxidation of sulphuric acid by the nascent anodic oxygen, assumes that persulphates are formed by anodic oxidation as given by the following reactions:

$$2HSO_4' + O + H_2O = H_2S_2O_8 + 2\ OH' \qquad (3)$$

$$2SO_4'' + O + H_2O = S_2O_8'' + 2\ OH' \qquad (4)$$

An increase in the anodic potential, on the basis of this theory would favour the per-sulphate formation; this has been experimentally verified.[4] That perdisulphuric acid can be prepared by the oxidation of sulphuric acid by nascent oxygen from hydrogen peroxide[7] is an additional support of Foerster's view.[5]

A more comprehensive theory of persulphate formation has been worked out by Muller,[4] who assumes that the primary anodic process is the discharge of OH'-ions which react with sulphuric acid to give perdisulphuric acid directly:

$$2H_2SO_4 + 2\ OH' = H_2S_2O_8 + 2\ H_2O + 2\ - \qquad (5)$$

This is followed by the secondary reactions

$$H_2S_2O_8 + H_2O = H_2SO_5 + H_2SO_4 \qquad (6)$$

$$H_2SO_5 + H_2O = H_2SO_4 + H_2O_2 \qquad (7)$$

$$H_2SO_5 + 2OH' = H_2SO_4 + H_2O + O_2 + 2\ - \qquad (8)$$

The $H_2S_2O_8$ formed is partly hydrolysed in successive steps to permono sulphuric or Caro's acid (H_2SO_5) and hydrogen peroxide. Besides, part of the Caro's acid acts as a depolariser at the anode by reacting with the discharged OH'-ions as shown in equation (8). With the progress of electrolysis the concentrations of $H_2S_2O_8$ and H_2SO_5 are greatly increased, and the main reactions taking place after some considerable time are those given by equations (5) and (8). In the case of sulphuric acid, a certain stage in the electrolysis may be reached at which the electric current is equally distributed between these two reactions so that as much $H_2S_2O_8$ as is formed by reaction (5) is converted into H_2SO_5 by reaction (7), and decomposed subsequently by the OH'-ions discharge (reaction (8)), at the anode. This corresponds to a "*steady state*" at which no fresh $H_2S_2O_8$ is formed even if the electrolysis is prolonged. The principal support for Muller's hypothesis[4] is that this "steady state" has been observed by numerous workers in the case of sulphuric acid.

It may be pointed out, however, that Muller's theory is based on the assumption that the main anodic processes (5) and (8) are the result of OH'-ion discharge; it is, however, different to understand how there could be any considerable concentration of OH′-ions in the highly acidic solutions that are required for persulphate formation.

The electrolysis of neutral solutions of sodium sulphate gives very low current efficiency (*cf.*, Table I). As may be expected from the modern theory of complete ionisation of electrolytes, it is likely that the concentration of the HSO_4'-ions in these solutions may be negligible; the whole of the sodium sulphate may be ionised into Na· and SO_4''-ions so that the prerequisite for persulphate formation is not satisfied. The observed low C.Es. may thus be explained. It is not improbable that these low C.Es. are due to the dissolved oxygen in the electrolyte. Results in Tables II and III show that an increase of the concentrations of sodium sulphate and sulphuric acid improve the C.E. markedly. Even normally, dilute sulphuric acid contains a fair percentage of HSO_4'-ions[8] so that the addition of sulphuric acid increases the HSO_4'-ions concentration which is favourable for persulphate formation. High C.Es. are thus observed at higher concentrations as recorded in Tables II and III.

When the anodic current density is increased the rate of discharge of the HSO_4'-ions is also increased, so that these ions are in a closely packed condition immediately after the discharge. This would facilitate their polymerisation and a high C.E. would result. Moreover, the discharge potential of the HSO_4'-ion is higher than that of SO_4''-ions and oxygen[4] and therefore, high anodic current densities would be favourable for its discharge. Results indicated in Table IV show that a rise in anodic current density up to 82·8 amps./dm^2 is followed by a corresponding rise in the C.E. At still higher current densities, however, the heating effect of the electric current probably becomes prominent and the C.E. consequently begins to fall.

Results recorded in Table VII show that the C.E. falls rapidly with rise of temperature (*cf.*, Table VII).

During the initial stages of the electrolysis, the concentration of the HSO_4'-ions in the electrolyte is a maximum. It decreases steadily when more and more of it is consumed by the formation of persulphate, so that the C.E. also begins to decrease with longer durations. Further complications due to the formation of perdisulphuric acid according to (5) and its decomposition by (6), (7) and (8) also set in. These have, in general, an unfavourable influence on the C.E. In the case of sulphuric acid, a 'steady state', as already indicated, is reached when a certain amount of electricity has been passed, after which, the amount of active oxygen in the electrolyte remains constant. Table VIII illustrates the influence of the duration of electrolysis on the C.E. and the active oxygen in the electrolysed solution.

After the passage of about two amp- -hrs. of electricity the separation of solid sodium persulphate begins to take place, which increases in bulk with the progress of electrolysis. Though the C.E. falls rapidly with greater durations, the active oxygen increases very regularly and our results do not indicate the attainment of a " steady state ". This may be due to the circumstance that, instead of the whole of the persulphate formed at the anode, being quantitatively destroyed after conversion into Caro's acid, a part or even the whole of it may be precipitated as the insoluble sodium salt. This is evidently not the condition which would correspond with Muller's concept of the ' steady state '.

The effect of addition agents on the C.E. according to Muller and others,[11] would be favourable if the Caro's acid produced by reaction (6) is destroyed either chemically or by over voltage effects produced by the ions of the addition agent on the anode. Increase of anodic potential would destroy Caro's acid and the reaction (8) may be inhibited; the electricity passed can thus be utilised solely for the production of $H_2S_2O_8$. The fluoride ion and the perchlorate ion have been found by Muller and Schellhaas[10] and Mazzucchelli[11] respectively, to raise the anode potential and an increase in the C.E. is consequently observed as recorded in Table X.

Factors such as cathodic current density (Table V), interelectrode distance (Table VI) and current concentration (Table IX) are found to have negligible influence on the C.E. The former two factors may be ineffective due probably to the comparative stability of the sodium persulphate towards reduction by cathodic hydrogen.

A diaphragm of porous material when used to separate the anolyte and catholyte is found to increase the C.E. to a very great extent, and in the presence of 1 gm. of HF in 100 c.c. of the anolyte, the C.E. is found to be very high (92·7%).

In conclusion the authors welcome this opportunity to express their very sincere thanks to Dr. S. S. Joshi, D.Sc. (London), University Professor and Head of the Department of Chemistry, Benares Hindu University for suggesting this problem, for the keen interest taken and the valuable guidance he has given during the course of this work.

SUMMARY

The optimum conditions for the electro-chemical formation of sodium persulphate from aqueous sodium sulphate have been investigated with respect to the bath composition, anodic and cathodic current densities, interelectrode distance, temperature, duration of the electrolysis, current con-

centration, the influence of " addition agents " and the use of a diaphragm. A strongly acidic bath favours the reaction. At the optimum temperature, *viz.*, 10° C. high anodic current densities up to 82·2 amps./dm^2 are advantageous. The process is complicated by the fact that after about 2 amp. hours the persalt tends to separate as a solid phase. Our results do not support Muller's hypothesis of a '*steady state*' in the corresponding sulphuric acid electrolysis. A current efficiency as high as 92·7% has been obtained with a diaphragm, HF as 'addition agent' and special concentration (*vide infra*) of the bath solution.

From a review of the various theories of persulphate formation, our results are in accord with Richardz's view, *viz.*, that persulphuric acid is produced by the polymerisation of discharged HSO_4'-ions at the anode.

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