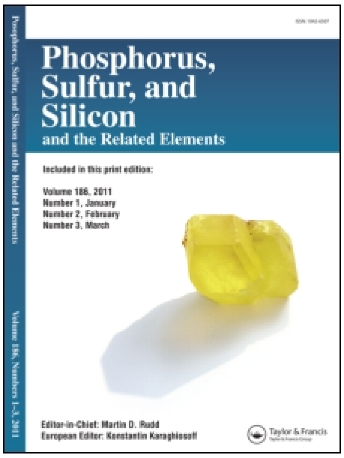

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ON THE NATURE OF SODIUM HYDROXYMETHANE SULFINATE IN AQUEOUS SOLUTION

by

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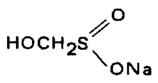
ABSTRACT

New data obtained on sodium hydroxymethane sulfinate in aqueous solution by voltammetry are presented, and discussed in relation to its chemistry. The most plausible explanation of the data would appear to be in terms of a tautomerism in solution, and such a thesis is compatible with the known behavior of this reducing agent.

Sulfoxylic acid (H_2SO_2) is a poorly characterized sulfur oxyacid with few derivatives. It has been described as both a reducing[1] and an oxidizing[2] agent, and this dual nature has been ascribed to the existence of two forms: symmetrical $S(OH)_2$, and unsymmetrical HSOOH (the sulfur analogue of formic acid).[3] The properties of the two forms have been reviewed by Lyons and Nickless.[4]

Studies on a crystalline derivative, "sodium formaldehyde sulfoxylate" ($HOCH_2SO_2Na$), by X-ray crystallography[5,6] and X-ray emission spectroscopy,[7-10] showed it to be a derivative of the unsymmetrical form, hence sodium hydroxymethanesulfinate (SHMS) 1.



1

HOCH$_2$O–S–ONa

2

However, many of the chemical data available on the reactions of SHMS conflict with this tetravalent sulfur structure 1, and attempts have been made to explain the discrepancies by postulating either hydrolysis of 1 in solution to give HCHO and HSO_2^-,[5,11,12] free radical decomposition to give the SO_2^- radical,[13] or a tautomerism in solution between forms 1 and 2.[5] The data which conflict with structure 1 most seriously are those from redox titrations.

SHMS develops full reducing power in acid solution[14] and has applications in the textile dyeing industry.[15,16] Oxidants such as iodine,[17-19] copper sulfate,[14,18-21] methylene blue,[14] KIO_3, KIO_4, H_2O_2[22] and chloramine-T[23] react quantitatively with SHMS in solution, and, depending on the oxidant, the hydroxy-methane sulfinate ion may be oxidized to either $HOCH_2SO_3^-$ or HCHO and $SO_4^=$, requiring two or four equivalents respectively.

Using oxidation number convention it appears that SHMS contains a sulfur atom in a +II oxidation state, and not in a +IV state as has been suggested.[5] However, a +II state is not consistent with a tetravalent structure, 1, which has led to the suggestion that SHMS may exist in solution as form 2,[22,24] a derivative of symmetrical sulfoxylic acid.

A possible explanation for the existence of two distinct forms of SHMS is that a pH-dependent tautomerism between structures 1 and 2 exists in solution. Barnett and Wilson[25] state that tautomerism may exist in covalent derivatives of sulfoxylic acid and may extend to the unionized acids and even to univalent ions. However, they consider it as inconceivable that the tautomerism should persist in dissociated sulfoxylic acid, since the ions $^-O{-}S{-}O^-$ and $^-O{-}S^-{=}O$ would be canonical extremes of the same mesomeric species. Spectroscopic data on some aromatic and aliphatic sulfinic acids have not allowed the question of tautomerism to be adequately answered,[26,27] although Wudl, *et al.*,[28] report that no tautomerism of methane sulfinic acid could be detected in deuteriochloroform at 25°C using nmr spectroscopy.

This communication presents new voltammetric data on the anodic wave of SHMS in aqueous solution, and attempts to explain the wave characteristics in terms of the possible species present in solution. The hydrolysis of SHMS, and the possibility of a tautomerism are investigated.

Experimental Section

The construction and operation of the rotating platinum microelectrode and the experimental conditions have been previously described.[29] The supporting electrolyte used was a series of McIlvaine buffers of constant ionic strength (1.0*M*).[30] The system was well buffered in the range pH 2 to pH 8. The pH was measured using a glass combination electrode (Radiometer GK2302C). All the data presented had a day-to-day reproducibility within ±3% under the controlled operating conditions outlined.[29]

Results and Discussion

A solution of SHMS gives rise to an anodic wave between 400 and 1000 mV (*vs.* S.C.E.) in the pH range 2 to 8 (Figure I). No wave was detected above pH 8 (in NaOH solution).

Analysis of the wave shape by the two tests outlined by Meites[31] showed that the electrode reaction giving rise to the wave is irreversible, *i.e.*,

(i) $|E_{3/4} - E_{1/4}| > 170\ \text{mV} \left(\gg \frac{56.4}{n}\ \text{mV}\right)$

and

(ii) a plot of E *vs.* $\log \frac{i_l - i}{i}$ is non-linear.

where E is the microelectrode potential, $E_{3/4}$ and $E_{1/4}$ are the potentials at which the wave current (i) is equal to three-fourths and one-fourth of the limiting current (i_l) respectively, and n is the number of electrons transferred.

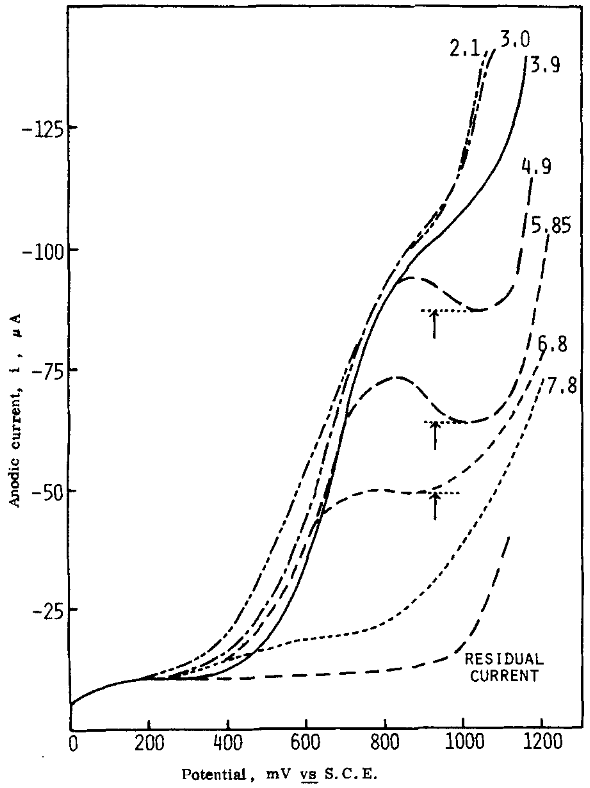


FIGURE I

Anodic waves of SHMS at pH values shown, 2 x 10^{-4} *F* SHMS. McIlvaine buffers, *I* = 1.0 *M*. Potential scan rate 0.2 V/min.

Linearity between the wave height and the concentration of SHMS was found to hold at all pH values investigated in this study excepting pH 4.9, in the concentration range 2 x 10^{-5} *F* to 2 x 10^{-4} *F* SHMS.

The occurrence of non-linearity at pH 4.9 corresponds to the appearance of a peak on the wave plateau. Neither the height nor the shape of this peak were affected by repeated recrystallization of the SHMS, addition of sulfide ions (1 x 10^{-5} *F* in the cell solution), or addition of maxima-suppressing agents such as Triton X-100, gelatin, or methyl red. The origin of the peak is probably a catalytic current which is often associated with organic sulfur compounds.[32,33]

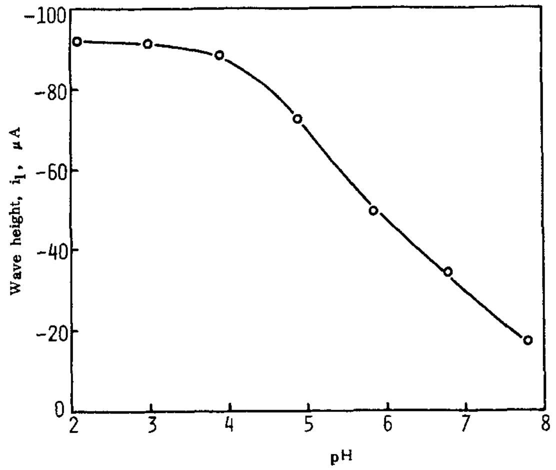


FIGURE II

Effect of pH on wave height 2 x 10^{-4} *F* SHMS. McIlvaine buffers, *I* = 1.0 *M*. Potential scan rate 0.2 V/min.

A plot of wave height against pH is shown in Figure II. The wave height for each wave was measured at +935 mV relative to the residual current curve. The choice of potential at which to measure the wave height has been discussed previously.[29] The wave height of the peaked waves was measured by taking the minimum of the peak as the wave plateau, as for a catalytic current.[33]

If hydrolysis of SHMS (eq 1) is postulated to explain the decrease in wave height with increasing pH, then equation 1 would be pH-dependent, and the anodic wave would arise from either $HOCH_2SO_2^-$ if the equilibrium shifted to the right with increasing pH, or to HSO_2^- if the equilibrium shifted to the left with increasing pH.

$$HOCH_2SO_2^- + H_2O \rightleftharpoons CH_2(OH)_2 + HSO_2^- \qquad (1)$$

As it is most probable that the reaction with formaldehyde and dithionite ions (eq 2) proceeds via hydrolysis of dithionite (eq 3)[19,34] and subsequent reaction of formaldehyde with the sulfoxylate and bisulfite ions, equation 1 would be expected to be reversible, and the addition of excess formaldehyde to the voltammetric cell solution would be expected to have a rapid and marked effect on the wave height.

$$S_2O_4^{=} + 2CH_2(OH)_2 \rightarrow HOCH_2SO_2^{-} + HOCH_2SO_3^{-} + H_2O \quad (2)$$

$$S_2O_4^{=} + H_2O \rightarrow HSO_2^{-} + HSO_3^{-} \quad (3)$$

However, no change in wave height was observed even up to 1.5 hr after the addition of a tenfold excess of formaldehyde.

Similarly, the possibility that free radicals such as $\cdot SO_2^{-}$ could give rise to the anodic wave must be discounted, as formaldehyde would be an efficient radical trap.

Alternatively, the decrease in wave height with increasing pH could be due to an acid-base dissociation, where the acid form gives rise to the anodic wave. (As no wave was detected above pH 8, the base form is assumed to be non-electroactive.)

If Figure II represents the dissociation of an electroactive acid, then the (voltammetric) pK_a of this acid would be approximately 6. This value is considerably higher than measured values for sulfinic acids which range from 1.2 (aromatic) or 2.2 (aliphatic).[26]

Polarographic determinations of pK_a can yield values higher than those obtained by other methods because base-form-proton reaction in the immediate vicinity of the electrode surface results in higher acid-form concentration than represented by the equilibrium conditions in the bulk solution.[35] However, as the half-wave potential appears to be independent of pH, it is highly probable that a proton transfer reaction does not precede the slowest step in the electrode reaction.[36]

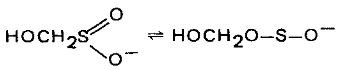
Therefore, if the pK_a value from Figure II is accepted, the species giving rise to the anodic wave cannot have the structure of the acid form of 1 which would have a pK_a of approximately 2, but it could have the structure of the acid form of 2 which would be a considerably weaker acid than 1.

A further possible explanation for Figure II may be suggested. Gossman[37] found a similar relationship between wave height and pH for the reduction of sulfurous acid at the dropping mercury electrode, and attributed this to the fact that the establishment of the equilibrium (eq 4) was slow relative to the electrode reaction.

$$H^+ + HSO_3^{-} \rightleftharpoons H_2SO_3 \quad (4)$$

However, Kolthoff and Miller[38] regard this explanation as not plausible because in the electrodeposition of hydrogen at the dropping mercury electrode from solutions of weak acids, the attainment of dissociation equilibrium is found to be faster than the rate of electroreduction. They explain this observation by proposing a tautomerism of sulfurous acid, one tautomer only being reducible at the dropping mercury electrode.

If a similar tautomerism is proposed for SHMS, then from the relationship between wave height and pH in Figure II it follows that only the free acid of 2 is electroactive. If the free acid of 1 were electroactive then because its pK_a would be approximately 2, no wave would be observed above pH 5. And as no wave was observed in alkaline solution, the bases 1 and 2 must be non-electroactive. The tautomerism may then be represented as:



$$HOCH_2S(=O)O^{-} \rightleftharpoons HOCH_2O{-}S{-}O^{-} \quad (5)$$

It is necessary to postulate that the attainment of equilibrium in equation 5 is slow relative to both electro-oxidation and the attainment of dissociation equilibrium of $HOCH_2OSOH$.

Such a tautomerism can account for the +II oxidation state inferred from data from redox titrations in acid solution, and for the apparent lack of reducing power of neutral and basic solutions of SHMS at room temperature.

It is possible that the free radicals that have been detected in acidic SHMS solutions[13] are intermediates in the tautomerism, as a C-S bond must be broken and a C–O bond formed.

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