Summary

1. An investigation of the effect of *p*H on the surface tension of solutions of sodium laurate and sodium nonylate shows that the surface tension is relatively high in basic and low in neutral solutions. This agrees with the idea that the long chain paraffin ions together with the electrostatically held positive "gegen" ions are adsorbed from the strongly basic solutions, while the much more surface active acid is adsorbed more greatly from the slightly basic or neutral solutions.

2. The presence of electrolytes, such as neutral salts, is found to lower greatly the surface tension, especially in the basic solutions. This indicates either that the adsorbed constituent is made more highly surface active, as by an effect upon the ionic atmosphere of the positive gegen ions, or there is an increase in the activity in the solution of the constituent which is adsorbed, or the nature of one of the adsorbed constituents is changed. The effect is not related in a simple way to the ionic strength, but exhibits a simple relation to the concentration of the electrolyte.

CHICAGO, ILL.
ITHACA, N. Y.
RECEIVED AUGUST 17, 1937

[CONTRIBUTION FROM THE COATES LABORATORY, LOUISIANA STATE UNIVERSITY]

The Oxidation of Aqueous Sulfide Solutions by Hypochlorites

BY A. R. CHOPPIN AND L. C. FAULKENBERRY

The oxidation of hydrogen sulfide results in the formation of sulfur,[1] sulfuric acid[2,3] or a mixture of these substances. No other intermediate products have been shown to be present except in the specific instance of the reaction between hydrogen sulfide and sulfur dioxide,[4] in which case polythionic acids[5] may be shown to be intermediate products. The oxidation of the alkali sulfides[6,7] is not so simple or direct[8] and may yield as end-products, sulfur, polysulfides, sulfites,[9,10] thiosulfites, or sulfates, depending upon the temperature and alkalinity of the solution. The chief difference in the oxidation of sulfide ions in acid or alkaline solutions lies in the formation of thiosulfites or polythionates. This is due no doubt to the greater stability of thiosulfates in alkali,[10,11] and its ready conversion to the polythionates[10,12,13] in acid solutions.

The *weight of opinion* seems to indicate that sulfur is the primary oxidation product of sulfides and with weak oxidants may be the only end-product in acid solution. In basic solution the hydroxyl ion becomes an important reactant[14,15] whose importance increases with concentration.

A great many of the intermediate products appearing in the oxidation of sulfides are due to secondary reactions. This is particularly true of the reactions involving oxidants such as the hypochlorites.[16,17]

Experimental

Iodometric methods were used in standardizing the solutions of sulfide and hypochlorite and to determine the oxidizing or reducing power of the mixtures. The quantity of sulfate produced was determined by a modification of the benzidine–hydrochloride method[18] which was substantiated in turn by the usual gravimetric methods. The oxidizing–reducing character of the solutions studied rendered the use of colorimetric indicators and the quinhydrone electrode impossible for determining the hydrogen ion concentration of the reaction medium. The glass electrode, however, proved quite satisfactory for this purpose and was used throughout the investigation.

Preliminary work[19] disclosed the fact that when equivalent quantities of sulfide and hypochlorite were mixed, the resulting solution showed a qualitative test for sulfide and sulfate and reduced a considerable quantity of iodine solution. This would indicate that sulfide and hypochlorite do not react equivalent for equivalent, or in a ratio of 1:1, but there is some reaction in effect whereby more hypochlorite is required than is indicated by the simple ratio.

---

(1) L. N. Vauquelin, *J. Pharm. Chem.*, [1] **11**, 126 (1824).

(2) L. J. Thenard, *Ann. chim. phys.*, [2] **8**, 478 (1818).

(3) G. Lunge and G. Billitz, *Dingler's J.*, **255**, 38 (1888).

(4) H. W. F. Wackenroder, *Arch. Pharm.*, **47**, 272; **48**, 140 (1846).

(5) H. Debus, *J. Chem. Soc.*, **53**, 278 (1888).

(6) E. Filhol, *Ann. chim. phys.*, [4] **28**, 529 (1873).

(7) A. Claussen and O. Bauer, *Ber.*, **16**, 1062 (1883).

(8) J. L. Bullock and G. S. Forbes, THIS JOURNAL, **55**, 232 (1933).

(9) S. A. Shchukarev and E. M. Kireeva-Tuzulakjova, *J. Gen. Chem.* (U. S. S. R.), **1**, No. 8-9, 1125 (1931).

(10) H. Bassett and R. G. Durrant, *J. Chem. Soc.*, 1401 (1927).

(11) A. Skrabal, *Z. Anal. Chem.*, **64**, 107 (1924).

(12) H. Debus, *Ann.*, **244**, 79 (1888).

(13) H. Hertlein, *Z. physik. Chem.*, **19**, 291 (1896).

(14) H. V. Tartar, THIS JOURNAL, **35**, 1741 (1913).

(15) M. Bodenstein and W. Karo, *Z. physik. Chem.*, **75**, 30 (1910).

(16) F. Raschig, "Schwefel- und Stickstoffstudien," Leipzig, 1924, p. 294.

(17) F. Dienert and F. Wanderbulcke, *Compt. rend.*, **169**, 29 (1919).

(18) F. P. Treadwell and W. T. Hall, "Analytical Chemistry," Vol. II, John Wiley and Sons, Inc., New York, 1935.

(19) J. G. Stevens, Master's Thesis, Louisiana State University, 1935.

The first work was to determine the equivalent reaction ratio when 5-ml. portions of exactly 0.05 *N* sodium sulfide were added consecutively to 50 ml. of exactly 0.05 *N* sodium hypochlorite solution. The excess oxidizing or reducing power and the basicity of the solutions were determined and qualitative tests were made for sulfide and sulfate. Colloidal sulfur was visibly evident throughout the tests. The results are shown in Table I.

TABLE I

TESTS FOR SULFIDE AND SULFATE UPON THE ADDITION OF SULFIDE TO HYPOCHLORITE. DETERMINATION OF CHANGES IN OXIDIZING POWER AND BASICITY

Temp., 24°. NaOCl constant at 50 ml.

Vol. Na_2S added, ml.	Ox. power 0.01 *N* sol. $Na_2S_2O_3$	Basicity HCl, ml.	Test sulfide	Test sulfate	Red. power 0.01 *N* sol. I_2
0	25.00	38.19	..	..	..
5	20.23	39.91	Neg.	Pos.	..
10	16.27	42.50	Neg.	Pos.	..
15	11.88	44.00	Neg.	Pos.	..
20	7.71	45.94	Neg.	Pos.	..
25	3.35	47.80	Neg.	Pos.	..
30	...	49.73	Pos.	Pos.	0.30
35	...	51.47	Pos.	Pos.	2.30
40	...	53.15	Pos.	Pos.	4.30
45	...	55.12	Pos.	Pos.	6.28
50	...	56.16	Pos.	Pos.	7.87

The data indicate that there is some mechanism in effect whereby the production of colloidal sulfur and sulfate occur simultaneously either by parallel or consecutive reactions and more than one equivalent of hypochlorite is necessary per equivalent of sulfide added. Irrespective of the mechanism, the stoichiometric relationships

$$NaOCl + Na_2S + H_2O = S + NaCl + 2NaOH \quad (1)$$

$$4NaOCl + Na_2S = 4NaCl + Na_2SO_4 \quad (2)$$

should hold. It may be stated with certainty that for the production of sulfur as the end-product of the reaction, one equivalent of hypochlorite will be required and for the production of sulfate as end-product, four equivalents of hypochlorite will be required per equivalent of sulfide, in which case the following ratios should hold

$$\frac{\text{Eq. NaOCl}}{\text{Equivalents Na}_2\text{S}} = 1 \text{ (for sulfur as end-product)}$$

$$\frac{\text{Equivalents NaOCl}}{\text{Equivalents Na}_2\text{S}} = 4 \text{ (for sulfate as end-product)}$$

Since sulfur and sulfate are produced simultaneously, one would expect the ratio to assume some value between one and four. The results of a series of investigations, using approximately equivalent concentrations of hypochlorite and sulfide are collected in Table II.

TABLE II

QUANTITATIVE PRODUCTION OF SULFUR AND SULFATE WHEN REACTANTS ARE OF APPROXIMATELY THE SAME CONCENTRATION

Temp. 25°, *p*H approximately 12, volume NaOCl constant at 50 milliliters

Normal NaOCl $\times 10^{-3}$	Concn. Na_2S $\times 10^{-3}$	Vol. Na_2S added ml.	Ratio equivalents $NaOCl/Na_2S$ reacted	Ratio S/SO_4 produced calcd.	Experimental detd.
4.740	5.00	10	1.84	2.57	2.53
4.740	5.00	15	1.85	2.53	2.52
4.740	5.00	20	1.82	2.66	2.60
4.740	5.00	25	1.83	2.62	2.64
51.50	56.10	10	1.87	2.45	2.44
51.50	56.10	15	1.84	2.57	2.61
51.50	56.10	20	1.88	2.41	2.26
51.50	56.10	25	1.88	2.41	2.40
104.2	112.00	10	1.82	2.66	2.69
104.2	112.00	15	1.86	2.49	2.40
104.2	112.00	20	1.84	2.57	2.52
104.2	112.00	25	1.83	2.62	2.66
225.6	232.10	10	1.86	2.49	2.32
225.6	232.10	15	1.85	2.53	2.52
225.6	232.10	20	1.81	2.70	2.50
225.6	232.10	25	1.86	2.49	2.44
		Average	1.846	2.546	

Under the conditions of the experiment it is evident that the ratio, equivalents of sulfide to equivalents of hypochlorite,, assumes an average value of 1.84 and is evidently constant for the various concentrations used. The next logical step would be to investigate the effect on the ratio when the reactants were not of the same or approximately the same concentration. These results are given in Table III.

TABLE III

EFFECT OF VARYING CONCENTRATION OF REACTANTS ON SULFUR AND SULFATE PRODUCTION

Temp. 25°, *p*H approximately 12, volume NaOCl constant at 50 ml., 0.00545 *N*

Concn. Na_2S added	Equivalents Na_2S reacted $\times 10^{-6}$	Equivalents NaOCl reacted $\times 10^{-6}$	Ratio $NaOCl/Na_2S$ reacted
0.2290	229	366	1.60
.1610	242	404	1.66
.1035	207	337	1.68
.0710	213	359	1.69
.0493	246.5	435	1.76
.00474	474	873	1.84

Volume Na_2S constant at 150 ml., 0.0203 *N*

NaOCl added			
0.0185	182.7	340	1.86
.0525	304.5	626	2.06
.098	203	440	2.12
.1503	203	469	2.31
.2024	203	537	2.664
.3050	203	602	2.96

Here the value of the ratio is not constant; high concentrations of hypochlorites result in the production of more sulfate (high ratio) and high concentrations of sulfide increase the production of sulfur (low ratio).

The assumption that sulfur and sulfate are the only end-products of the reaction has not been established by the data so far presented. If the assumption is correct, one can calculate the quantity of sulfur and sulfate that should be produced in any mixture of sulfide and hypochlorite from the ratio of these reactants consumed in the course of the reaction. Starting with one mole of sodium sulfide and letting X mole go to sulfur and Y mole to sulfate, we can obtain two simultaneous equations,

$$X + Y = 1 \text{ (with respect to sulfide)}$$
$$X + 4Y = \text{ratio with respect to hypochlorite}$$

from which (using the ratio for 0.2 N solutions in Table II) we find

$$X + Y = 1$$
$$X + 4Y = 1.86$$

for which $X = 0.7133$ mole and $Y = 0.2867$ mole. The reactants should yield sulfur and sulfate in the ratio $S/SO_4 = 2.49$ moles. The calculated and experimentally determined values for the concentrations studied are shown in the last two columns of Table II. The agreement between these values is well within the limit of experimental error.

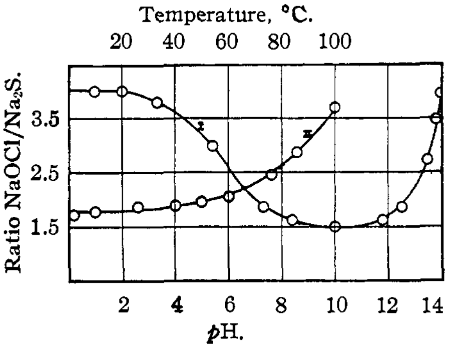

Fig. 1.—Effect on sulfate production: I, pH ratio; II, temperature ratio.

Quite early in the work it became apparent that such factors as temperature, standing time, rate of addition and the hydrogen ion concentration altered the ratio of sulfur and sulfate produced. These four factors have their influence as a result of secondary reactions involving the re-solution of colloidal sulfur. Sodium hydroxide is known to react with sulfur[14,20,21] at ordinary temperatures but the rate of reaction is slow and depends upon the concentration of the alkali. Inasmuch as it seemed advisable to have definite information regarding these effects upon the reactions studied, we carried out experiments to show the effect of increased alkali concentrations and temperature on colloidal sulfur. The reaction may be represented by the equation

$$6NaOH + 8S = 2Na_2S_3 + Na_2S_2O_3 + 3H_2O$$

and its course may be followed by determining the increase in reducing power iodometrically. The results of our investigation are shown graphically in Figs. 1 and 2 and in Table IV.

TABLE IV

EFFECT OF TEMPERATURE ON S/SO_4 RATIO

EFFECT OF TEMPERATURE ON SULFUR AND SULFATE PRODUCTION

Solutions: 50 ml. 0.0515 NaOCl, 5–25 ml. 0.0561 Na_2S (5 ml. additions), pH approximately 12

Temp., °C.	Ratio NaOCl/Na₂S Equivalents reacted
0	1.72
10	1.79
25	1.86
40	1.90
50	1.98
60	2.08
75	2.45
85	2.88
100 (Boil)	3.66

It will be noted that high temperatures increase the ratio (Fig. 1), hence the sulfate production.

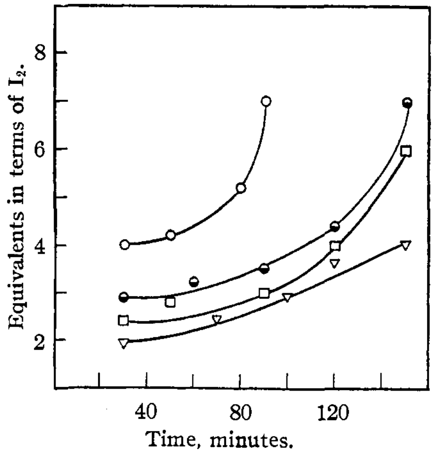

Fig. 2.—Rate of solution of sulfur in sodium hydroxide at 25°: □, 0 N; ▽, 0.1 N; ○, 2.0 N; ◒, 1.0 N.

Figure 2 shows the increased rate of reaction of sulfur with increase in alkali concentration. The standing time and rate of addition influence is also due to this secondary reaction involving the re-

---

(20) M. J. Fordos and A. Gelis, *Compt. rend.*, **31**, 702 (1850).

(21) T. Salzer, *Arch. Pharm.*, **231**, 663 (1893).

solution of the sulfur and its subsequent oxidation by the excess hypochlorite.

The effect of hydrogen ion concentration on the relative quantities of sulfur and sulfate produced was observed with the aid of buffer solutions. In this work it was necessary to use rather dilute solutions in order to prevent the loss of hydrogen sulfide and chlorine in acid solution. From ten to twenty-five milliliters of 0.0581 *N* hypochlorite were added to 100 milliliters of the desired buffer solution and varying quantities of 0.0516 sodium sulfide added. The *p*H of the solution was then checked with the glass electrode except for the very high values. In the solutions of *p*H approximately 14, 12.8 and 13.4, the *p*H of the alkali was determined with a hydrogen electrode. Inasmuch as both the reactant solutions are slightly alkaline, having *p*H values of 11.8 and 11.7 for sulfide and hypochlorite, respectively, the *p*H of the very alkaline solutions did not alter appreciably upon the addition of the comparatively small volumes of the reactants. The results of the experiments are reproduced in Table V and Fig. 1, Curve I.

Table V

Effect of *p*H on the Ratio $NaOCl/Na_2S$

*p*H	Equivalents $NaOCl/Na_2S$	Electrode	Buffer solution
14 (appx.)	3.98	H_2	NaOH 3 *N*
13.8	3.71	H_2	NaOH 1.5 *N*
13.4	2.72	H_2	NaOH 0.4 *N*
12.5	1.86	Glass	NaOH–NaCl Glycine
11.8	1.67	Glass	$NaOH–H_3BO_3$
10.0	1.50	Glass	$NaOH–H_3BO_3$
8.4	1.63	Glass	$NaOH–H_3BO_3$
7.3	1.85	Glass	$NaOH–KH_2PO_4$
5.4	3.00	Glass	$NaOH–KHC_8H_4O_4$
3.3	3.74	Glass	$NaOH–KHC_8H_4O_4$
2.00	4.01	Glass	HCl–KCl
1.00	4.01	Glass	HCl–KCl

The ratio of equivalents of hypochlorite to equivalents of sulfide and hence the ratio of sulfate to sulfur produced reaches a minimum value at a *p*H of 10, gradually increasing on both sides of this point. Toward the acid end of the curve there is a gradual increase in the formation of sulfate up to a *p*H of 2.00. At and below this point there is a quantitative conversion of sulfide to sulfate. On the more alkaline side of *p*H 10 there is an even sharper increase in the proportion of sulfate formed, reaching the theoretical limit of 4, within experimental error, indicating a quantitative conversion to sulfate at *p*H 13.8 (1.5 *N* sodium hydroxide).

The oxidation of sulfide with hypochlorite is accompanied by an increase in the alkalinity of the solution. Accordingly, reaction (1) may be postulated as the initial reaction. A better realization of this mechanism is obtained with slow acting oxidants, *e. g.*, the work of Bullock and Forbes.[8] These investigators oxidized sulfide with certain aromatic nitro compounds and definitely showed sulfur to be their primary though not their final product. Obviously, since the ratio of hypochlorite to sulfide reacting lies somewhere between the limiting values one and four for solutions between *p*H 2 and 14, sulfur and sulfate are being produced simultaneously. Since the primary reaction results in the formation of sulfur

$$Na_2S + NaOCl + H_2O = NaCl + NaOH$$

the sulfate formation must be due to secondary reactions. The sulfur set free in the active state may react in either of two ways. It may combine with another atom of sulfur or it may react with a molecule of sodium hypochlorite as follows

$$S + S = S_2 \qquad (3)$$

$$S + 3NaOCl + H_2O = H_2SO_4 + 3NaCl \qquad (4)$$

Reaction (3) is not, of course, limited to the formation of diatomic sulfur. Equation (4) is probably not kinetically correct since it is shown as a quinquimolecular reaction. It can probably be represented more accurately by

$$S + NaOCl = SO + NaCl \qquad (5)$$

$$SO + H_2O = H_2SO_2 \qquad (6)$$

$$H_2SO_2 + NaOCl = H_2SO_3 + NaCl \qquad (7)$$

$$H_2SO_3 + NaOCl = H_2SO_4 + NaCl \qquad (8)$$

The experimental results from a kinetic point of view are explained in terms of reactions (3) and (5–8). The constancy of the ratio of sulfur to sulfate as long as the reactants are of essentially the same concentration is also explained, inasmuch as the square of the sulfur concentration is mathematically equivalent to the product of the hypochlorite and sulfur concentrations under such circumstances. The mechanism appears to explain successfully variations due to changes in concentration.

To explain the increased sulfate production on both sides of the minimum (Curve I, Fig. 1) it is necessary to consider two distinct reactions whereby the colloidal sulfur is returned to solution. At high *p*H values sodium hydroxide reacts with sulfur, producing sulfides and thiosulfate. The reaction is one of autoöxidation with no net gain in the oxidizing or reducing power of the solution. As the alkalinity of the solution increases the rate of solution of the sulfur increases, according to

$$6NaOH + 8S = 2Na_2S_3 + Na_2S_2O_3 + 3H_2O$$

and at the limiting alkalinity of 3 normal with respect to sodium hydroxide, colloidal sulfur is redissolved as rapidly as it is produced and sulfate is the only product of the reaction (see Table V).

Goldschmidt attributes the increased oxidizing power of hypochlorite in acid solution to the presence of chlorine monoxide. Chlorine monoxide may also function as a reagent for the re-solution of colloidal sulfur, according to the equation

$$Cl_2O + S = SO + Cl_2$$

In solutions of sufficiently high hydrogen ion concentration (*p*H 2) this action is sufficiently rapid so that sulfate is again the only end-product of the reaction. From a kinetic point of view the experimental results agree with these postulates and the free energy values for the various equations proposed indicate that all of the major reactions are thermodynamically possible.

Conclusions

When sulfide solutions react with an excess of hypochlorite, sulfur and sulfate are formed as end-products in quantities depending upon the concentration of the reactants, the temperature, and hydrogen ion concentration of the reaction medium. When the reactants are of approximately the same concentration the relative amount of sulfur and sulfate produced are constant for dilute solutions. If there is a wide divergence in concentration of the sulfide and hypochlorite, the ratio of sulfur to sulfate produced is altered. High sulfide concentrations increase the formation of sulfur and high hypochlorite concentrations increase the sulfate formation.

An increase in temperature increases the sulfate formation, due to an increase in the rate of solution of colloidal sulfate.

There is a distinct minimum in the production of sulfate in the region of a *p*H of 10 with increased sulfate formation at values above and below this point. This effect is also probably due to an increase in the rate of solution of colloidal sulfur.

BATON ROUGE, LA. RECEIVED MAY 25, 1937

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

Phenanthrene Derivatives. VII. The Cyclization of β-Phenanthrylpropionic Acids

BY W. E. BACHMANN AND M. C. KLOETZEL

Four of the five possible β-phenanthrylpropionic acids have been prepared and subjected to cyclization in the form of their acid chlorides; these are the acids containing the 1-, 2-, 3- and 10-phenanthryl groups. The acids were obtained by means of the malonic ester synthesis and also by reduction of the corresponding β-phenanthrylacrylic acids. The products prepared by the two methods proved to be identical in each instance.

Mosettig and van de Kamp[1] prepared 2-, 3-, and 10-phenanthrylcarbinol by catalytic reduction of the corresponding phenanthraldehydes. We have carried out the reduction of these aldehydes and also of 1-phenanthraldehyde by means of the bromomagnesium salt of benzohydrol[2] and have obtained the phenanthrylcarbinols in excellent yields.

$$C_{14}H_9CHO + (C_6H_5)_2CHOMgBr = C_{14}H_9CH_2OMgBr + (C_6H_5)_2CO$$

Condensation of the phenanthrylmethyl bromides with sodiomalonic ester gave 60–70% yields of the phenanthrylisosuccinic acid esters except in the case of the 2-phenanthrylmethyl bromide, which gave a poor yield of the ester. By decarboxylation of the phenanthrylisosuccinic acids the β-phenanthrylpropionic acids were readily obtained. In the second procedure the phenanthraldehyde was condensed with malonic acid in the presence of pyridine; the reaction proceeded rapidly with the formation of the β-phenanthrylacrylic acid (I, for example) in nearly quantitative yield. By means of sodium amalgam and water, the β-phenanthrylacrylic acids were reduced to the β-phenanthrylpropionic acids (II, for example).

Cyclization of the acid chloride of β-(1-phenanthryl)-propionic acid by means of aluminum chloride in nitrobenzene yielded two cyclic ketones, 3′-keto-1,2-cyclopentenophenanthrene (III)

---

(1) Mosettig and van de Kamp, THIS JOURNAL, **55**, 2995 (1933).

(2) Gomberg and Bachmann, *ibid.*, **52**, 4967 (1930); Shankland and Gomberg, *ibid.*, **52**, 4973 (1930).