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THE BASE-CATALYSED OXIDATION OF ALIPHATIC AND AROMATIC THIOLS AND DISULPHIDES TO SULPHONIC ACIDS

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Abstract—The base-catalysed oxidation of several aliphatic and aromatic thiols and disulphides has been studied under one atmosphere pressure of oxygen at 23·5 and 80° in various alkali metal hydroxide–dipolar solvent systems. Excellent yields of the corresponding sulphonic acids were obtained under these reaction conditions. The preferred solvent for these reactions was found to be hexamethylphosphoramide (HMPA). The synthetic limitations and restrictions accompanying these reactions are outlined and discussed.

INTRODUCTION

IN THE presence of strong oxidizing agents such as barium permanganate, boiling nitric acid and hydrogen peroxide thiols are converted to sulphonic acids in yields varying from 30 to 90%.[1–4] The low temperature autoxidation of thiols in neutral media does not take place in the absence of added radical initiators such as peroxides, trace metals or UV light and, in the absence of olefins, the primary oxidation products are disulphides.[5] The base-catalysed autoxidation of thiols to disulphides occurs at low temperatures and the active species is the anion, $RS^{\ominus}$.[6] Previous studies in these laboratories have demonstrated that dipolar solvents markedly accelerate the low temperature, base-catalysed oxidation of thiols to disulphides.[7–9] In a more recent communication,[10] we reported that at high levels of thiol conversion, oxidation to sulphonic acids occured in potassium hydroxide—dimethylformamide. This new oxidation reaction confirmed earlier speculations by Xan *et al.*[11] The present manuscript presents detailed data on the base-catalysed oxidation of aliphatic and aromatic thiols and disulphides to sulphonic acids in various heterogeneous alkali metal hydroxide–dipolar solvent systems. Related factors such as the effect of protic species and oxygen partial pressure on the yield of acid have also been studied.

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[1] P. A. Levene and L. A. Mikeska, *J. Biol. Chem.* **75**, 587 (1927).

[2] P. A. Levene and L. A. Mikeska, *J. Biol. Chem.* **65**, 518 (1925).

[3] D. L. Vivian and E. E. Reid, *J. Amer. Chem. Soc.* **53**, 3407 (1931).

[4] D. Schöberl, *Z. Phys. Chem.* **216**, 193 (1933).

[5] E. E. Reid, *Organic Chemistry of Bivalent Sulphur* **1**, Chap. 1. Chemical Publishing Co., New York, N.Y. (1958).

[6] For a review see A. A. Oswald and T. J. Wallace, Chapter on the *Anionic Oxidation of Thiols and the Co-Oxidation of Thiols with Olefins in Organic Sulphur Compounds* (Edited by N. Kharasch), II, Pergamon Press, New York, N.Y. (1965).

[7] T. J. Wallace and A. Schriesheim, *J. Org. Chem.* **27**, 1514 (1962).

[8] T. J. Wallace, J. M. Miller, N. Pobiner and A. Schriesheim, *Proc. Chem. Soc.* 384 (1962).

[9] T. J. Wallace, A. Schriesheim and W. Bartok, *J. Org. Chem.* **28**, 1311 (1963).

[10] T. J. Wallace and A. Schriesheim, *Tetrahedron Letters* No. 17, 1131 (1963).

[11] J. Xan, E. A. Wilson, L. D. Roberts and N. N. Horton, *J. Amer. Chem. Soc.* **63**, 1139 (1941).

RESULTS

The base-catalysed oxidation of several aliphatic acid aromatic thiols and disulphides by molecular oxygen has been studied in various alkali metal hydroxide–dipolar solvent systems in the temperature range of 23·5 to 80°. Oxidation experiments were carried out at an oxygen partial pressure of one atmosphere using the method described in the experimental section. The alkali metal hydroxide–dipolar solvent mixtures were, in all cases, heterogeneous catalyst systems. Unreacted thiol and the amount of disulphides produced were determined by initial titration with silver nitrate, reduction of the disulphide to thiol in a zinc–acetic acid media, and titration of the increased thiol concentration by silver nitrate. Subsequent correction of the initial thiol concentration yielded the amount of thiol equivalent to disulphide. Quantitative data on the sulphonic acid produced was determined by either an ion-exchange IR or UV comparison to an authentic sample of the acid using standard calibration curves.

The oxidation of 1-butanethiol to 1-butanesulphonic acid was used as a model reaction to determine the effect of base and solvent on reactions of this general type. Excess potassium and sodium hydroxide were employed as the base and the dipolar solvents investigated were dimethylformamide (DMF), hexamethylphosphoramide (HMPA) and tetramethylurea (TMU). The reaction conditions employed and the results obtained from this study are summarized in Table 1. Data obtained in potassium hydroxide–pyridine and sodium methoxide–methanol are also included. As indicated, the yield of 1-butanesulphonic acid in DMF and HMPA varied from 88–95 mole % depending upon the reaction time and temperature employed.[12] Only small quantities of n-butyl disulphide were produced in these reactions. TMU was not as effective a solvent since only a 64% yield of acid was obtained after 23 hr of oxidation at 23·5°. In methanol, the only product observed was the disulphide and in pyridine, which is an aprotic solvent of low dielectric, the ratio of disulphide to acid was 3 after 18 hr of oxidation at 80°. Thus, the dipolar solvents have a marked effect on this reaction. It is also obvious that potassium and sodium hydroxide are equally effective as the base. Finally, the material balance between thiol converted and the amount of

TABLE 1. EFFECT OF SOLVENT AND BASE ON THE OXIDATION OF 1-C_4H_9SH TO 1-$C_4H_9SO_3H$

1-C_4H_9SH (mole)	Solvent[a]	Base	Base/ RSH	T., °C.	% Conversion of RSH	% Yield[b] of RSO_3H	% Yield[b] of R_2S_2	Time, hr
0·20	CH_3OH	NaOMe	2	23·5	—	—	85	7
0·025	HMPA	KOH	4	23·5	96·8	95·0	3·1	24·5
0·025	HMPA	KOH	4	23·5	95·1	94·9	0·9	21·5
0·025	HMPA	KOH	4	80	100	100	—	23
0·0126	HMPA	KOH	4	80	99	96	0·8	6
0·025	DMF	KOH	4	23·5	98·2	88	9·3	17·5
0·025	HMPA	NaOH	4	23·5	97·3	90·3	8·5	24
0·025	HMPA	NaOH	4	80	90	92	0·9	18·5
0·025	DMF	NaOH	4	23·5	93·7	66·6	23·5	18·5
0·025	TMU	KOH	4	23·5	92·6	64·3	28·1	23
0·026	Pyridine	KOH	4	80	82·5	20	64	18

[a] HMPA = hexamethylphosphoramide; DMF = dimethylformamide, TMU = tetramethylurea.
[b] Moles product/theoretical moles × 100.

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[12] It should be emphasized at this point that all base-solvent systems were heterogeneous.

disulphide and acid produced was excellent in all cases and this is further confirmation of the accuracy of the analytical techniques employed.

The oxidation of other thiols was investigated in potassium hydroxide–HMPA at a base to thiol ratio of 4. Benzenethiol, *p*-toluenethiol, *o*-toluenethiol, and 2-carboxybenzenethiol were converted to their corresponding sulphonic acids in 93 to 96 % yields in KOH–HMPA at 80°. These studies are summarized in Table 2. Good yields of these acids were also obtained at 23·5°. 1-Hexadecanethiol, which is rather high in mol. wt., did not oxidize readily at 23·5°. At 80°, a 96 % yield of 1-hexadecanesulphonic acid was obtained in 21 hr. Two aliphatic thiols which contain a tertiary-SH group were also studied. 2-Methyl-2-propanethiol was oxidized at 23·5° to 2-methyl-2-propanesulphonic acid in 72 % yield after 12 hr. 2,2-Dipentyl-1-hexanethiol was converted to 2,2-dipentyl-1-hexane-sulphonic acid in 63 % yield after 42 hr of oxidation at 80°. Thus, sterically hindered thiol groups can also be oxidized reasonably well under these conditions.

Table 2. Summary of other thiol oxidation studies using potassium hydroxide

RSH (mole)	Solvent	KOH/RSH	T, °C.	% Conversion of RSH	% Yield[a] of RSO_3H	% Yield[a] of R_2S_2	Time, hr
C_6H_5SH (0·025)	HMPA	4	23·5	99	90	6·4	12
C_6H_5SH (0·025)	DMF	4	23·5	100	91	4·7	22
C_6H_5SH	HMPA	4	80	98	92·5	3·8	29
o-$CH_3C_6H_4SH$ (0·025)	HMPA	4	23·5	100	80	21	24
o-$CH_3C_6H_4SH$[b] (0·025)	HMPA	4	80	99	95	4·5	24
p-$CH_3C_6H_4SH$ (0·025)	HMPA	4	80	100	94	6·4	24
o-HOOC—C_6H_4SH (0·025)	HMPA	4	80	99	96	4·6	24
$(CH_3)_3CSH$ (0·024)	HMPA	4	23·5	99	71·6	25	12
1-$C_{16}H_{33}SH$ (0·025)	HMPA	4	23·5	91·6	38·4	55·6	24
1-$C_{16}H_{33}SH$ (0·025)	HMPA	4	80	97·5	96	0·5	21
$(C_5H_{11})_3CSH$	HMPA	4	80	100	62·5	37·4	42

[a] Moles product/theoretical moles × 100.

[b] No *o*-sulphobenzoic acid was formed.

Since these systems are heterogeneous in nature, no attempt to obtain actual kinetic data was made. However, the relative order of thiol reactivity can be obtained by comparing the initial rates of oxygen consumption. In Fig. 1 the initial moles of oxygen consumed/mole of thiol are plotted as a function of time for 1-butanethiol, benzenethiol, and 1-hexadecanethiol. At 23·5°. the order of thiol reactivity was 1-$C_4H_9SH > C_6H_5SH >$ 1-$C_{16}H_{33}SH$. All rates were fastest in the initial stages of reaction and decreased with time. At 80°, the rate of oxidation for the high mol. wt. thiol was midway between that observed for 1-butane- and benzenethiol at 23·5°. Thus, high mol. wt. aliphatic thiols, e.g., C_{16}-thiols, can be oxidized at rates comparable to their lower molecular weight analogues at higher temperatures.

The above results suggest that disulphides are among the initial oxidation products formed. The oxidation of these species is also a new reaction. Thus, it was desirable to investigate specifically the oxidation of a few representative disulphides under these reaction conditions. These studies are summarized in Table 3. n-Butyl- and phenyl disulphides were oxidized to their corresponding sulphonic acids in high yields between 23·5 and 80° in both DMF and HMPA. The base to disulphide ratio in all cases was 8.

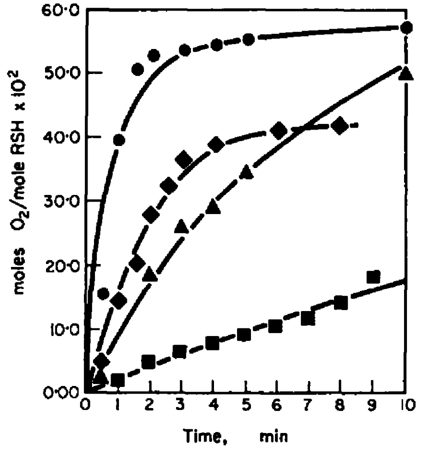

FIG. 1. Dependence of rate of oxygen consumption on mercaptan type

● 1-C_4H_9SH in KOH/HMPA (23·5°)
▲ C_6H_5SH in KOH/HMPA (23·5°)
■ 1-$C_{16}H_{33}SH$ in KOH/HMPA (23·5°)
◆ 1-$C_{16}H_{33}SH$ in KOH/HMPA (80°)

Even the more sterically hindered disulphide, *o*-tolyl disulphide, gave an excellent yield of *o*-toluenesulphonic acid in KOH–HMPA at 80°. Thus, these reactions also proceed smoothly under these conditions. Unlike the thiols, the aromatic disulphides were found to be more reactive than aliphatic disulphides. This point is emphasized in Fig. 2 by comparing the rates of oxygen consumption observed for phenyl disulphide and n-butyl disulphide in KOH–HMPA at 23·5°.

TABLE 3. SUMMARY OF BASE-CATALYSED DISULPHIDE OXIDATION STUDIES

R_2S_2 (mole)	Solvent	Base	Base/ R_2S_2	T, °C.	% Conversion of R_2S_2	% Yield of RSO_3H	% Yield of RSH	Time, hr
n-Bu_2S_2 (0·0125)	HMPA	KOH	8	23·5	98	92·3	3	41
n-Bu_2S_2 (0·0125)	HMPA	KOH	8	80	96	97	0	45
n-Bu_2S_2 (0·0125)	DMF	KOH	8	23·5	87·7	88·1	0	45
n-Bu_2S_2 (0·0125)	HMPA	NaOH	8	80	95	94·2	0·9	35
$(C_6H_5)_2S_2$ (0·0125)	HMPA	KOH	8	23·5	97·7	88·1	—	22
$(C_6H_5)_2S_2$ (0·0125)	HMPA	KOH	8	80	98	99	0	22·5
$(C_6H_5)_2S_2$ (0·0125)	DMF	KOH	8	23·5	98·5	90	0·3	40
(o-CH_3—$C_6H_4)_2S_2$	HMPA	KOH	8	80	98	98	0	23

As indicated previously, the predominant oxidation product from thiols in protic solvents is the disulphide. For mechanistic purposes, it was desirable to ascertain how protic species effect the base-catalysed oxidation of thiols and disulphides in dipolar-aprotic media. Thus, the oxidation of 1-butanethiol and n-butyl disulphide was studied at 80° in several KOH–HMPA–water mixtures. The total reaction time in all experiments was 5 hr. These results are summarized in Figs. 3 and 4. As shown in Fig. 3, dilution with 10 vol % water had little effect on the reaction. Beyond this point, however, there is a sharp decrease in acid selectivity. In the presence of 30 vol % water, the mole % yield of acid was decreased to 42%. The effect of water on the mole % conversion of the disulphide was similar. In the presence of 30 vol % water, the conversion of the disulphide dropped to 46%. At 23·5°, the effect of water was even greater. As shown in Table 4, addition of 10 vol. % water to the KOH–HMPA system decreased the yield of sulphonic acid from 95 to 54 mole %. Thus, protic media inhibits the oxidation of the disulphide.

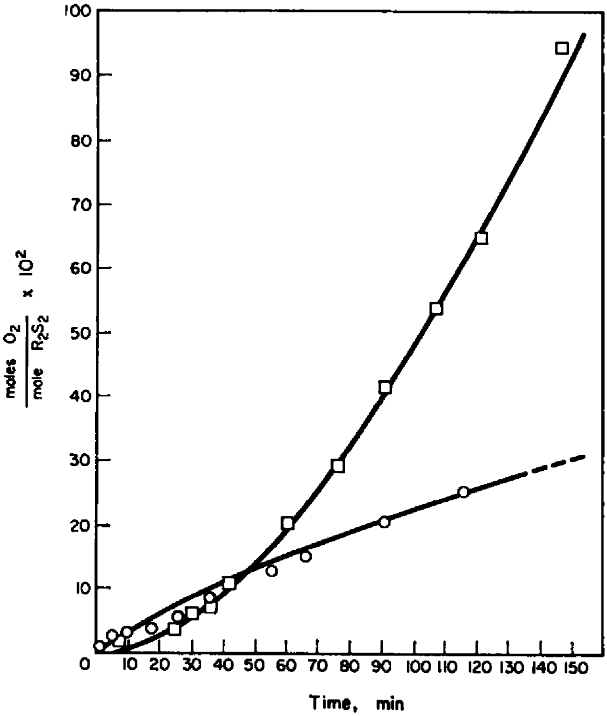

FIG. 2. Rates of oxygen consumption for n-butyl disulphide and phenyl disulphide in KOH/HMPA at 23·5°
○ $(n\text{-}C_4H_9)_2S_2$
□ $(C_6H_5)_2S_2$

Finally, a brief study on the use of air as the oxidant as opposed to pure oxygen was made (Table 5). In the closed system, the initial rates of oxygen consumption were comparable but the final yield or acid was decreased by 20 mole %. A continuous flow of air (15 ml/min) through a perforated disc in the reaction flask produced the same yield of acid obtained in the presence of pure oxygen.

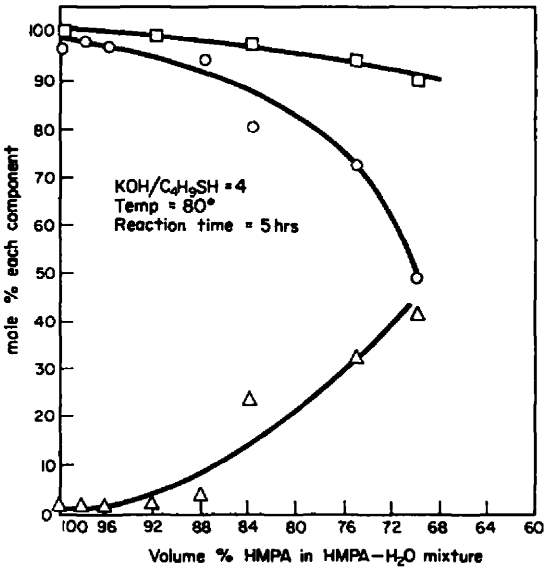

FIG. 3. Effect of H_2O dilution on the oxidation of 1-C_4H_9SH to 1-$C_4H_9SO_3H$ in KOH/HMPA at 80°.

○ Mole % yield 1-$C_4H_9SO_3H$
△ Mole % yield n-$(C_4H_9)_2S_2$
☐ Mole % 1-C_4H_9SH reacted (conversion)

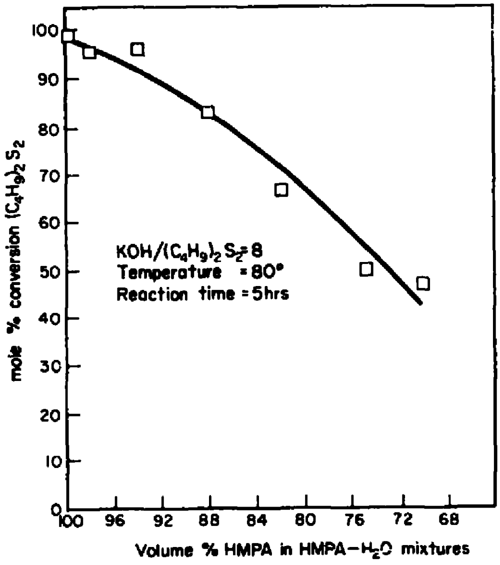

FIG. 4. Effect of H_2O dilution on the oxidation of n-$(C_4H_9)_2S_2$ in KOH/HMPA at 80°.

TABLE 4. EFFECT OF H_2O DILUTION ON THE OXIDATION OF 1-C_4H_9SH AT 23·5°

0·0125 mole 1-C_4H_9SH
KOH/n-C_4H_9SH = 4
1 atm. O_2
HMPA—H_2O
5 hr

Volume % HMPA	% C_4H_9SH Conversion	% Yield of RSO_3H	% Yield R_2S_2
90	95·5	54·1	40·9
80	99	48·2	51·8

TABLE 5. EFFECT OF OXYGEN PARTIAL PRESSURE ON THE YIELD OF 1-$C_4H_9SO_3H$

0·025 mole n-C_4H_9SH
KOH/C_4H_9SH = 4
23·5°

Oxidant	System	Mole % Yield 1-$C_4H_9SO_3H$	Time, hr.
O_2	Closed	95	21·5–24·5
Air	Closed	76·2	21·5
Air	Flow-15 cc./min.	94	23

DISCUSSION

Based on the results which have been summarized in Tables 1, 2 and 3, it seems reasonable to conclude that the low temperature, base-catalysed oxidation of aliphatic and aromatic thiols and disulphides to sulphonic acids is a general reaction that proceeds in excellent yields. Further, it is obvious that dipolar solvents are the preferred media for carrying out reactions of this type. The latter finding is consistent with other recent studies in the general area of base catalysis,[13,14] The exact role of the solvent with respect to the mechanism of the reaction will be discussed shortly. However, some comments on the limitations of the reaction with respect to the base employed and the type of thiol or disulphide that can be oxidized to a sulphonic acid should first be made.

With respect to the thiol and disulphide, both aliphatic and aromatic compounds can be oxidized to their corresponding sulphonic acids in high yields. Thiols and disulphides which contain acidic alpha-hydrogen atoms undergo side reactions in the presence and absence of oxygen. For example, α-toluenethiol and benzyl disulphide gave appreciable yields of benzoic acid when oxidized at room temperature in the presence of potassium hydroxide and a dipolar solvent.[15] In the presence of a stronger base such as potassium-t-butoxide, the yield of carboxylic acid increased. α-Toluenesulphonic acid was also oxidized readily to benzoic acid in the presence of potassium-t-butoxide. In the absence of oxygen, benzyl disulphide undergoes a carbanion-rearrangement-elimination reaction to product stilbene.[16] Thus, thiols and disulphides

[13] A. J. Parker, *Quart. Revs.* **16,** 163 (1962).

[14] D. J. Cram, *Chem. Eng. News* p. 92, Aug. 19 (1963).

[15] For details of these studies see T. J. Wallace, H. Pobiner and A. Schriesheim, *J. Org. Chem.* **29,** 888 (1964).

[16] T. J. Wallace, H. Pobiner, J. E. Hoffmann and A. Schriesheim, *Proc. Chem. Soc.* 137 (1963); *J. Chem. Soc.* 1271 (1965).

containing acidic alpha-hydrogens are capable of undergoing numerous reactions in these base-solvent systems.

The limitations of this oxidation technique with respect to the base employed, pertains to the apliphatic thiols and disulphides. In the presence of a strong base, e.g., potassium-t-butoxide, and a dipolar solvent, aliphatic thiols and disulphides undergo beta-elimination reactions to produce olefins by loss of either a sulphide or a mercaptide ion,[17]

$$R\overset{\ominus}{C}H-CH_2-\overset{\ominus}{S}\longrightarrow RCH=CH_2+\overset{⊜}{S} \quad (1)$$

$$R\overset{\ominus}{C}H-CH_2-S-S-R\longrightarrow RCH=CH_2+R\overset{\ominus}{S_2} \quad (2)$$

Disulphides are more suspectible to this reaction than thiols and the reaction has been observed with n-butyl disulphide. Side reactions with the aromatic derivatives are a minimum. Even in the presence of excess base at 80°, the thiol group and disulphide linkage are oxidized in preference to alkyl groups on the aromatic nucleus.

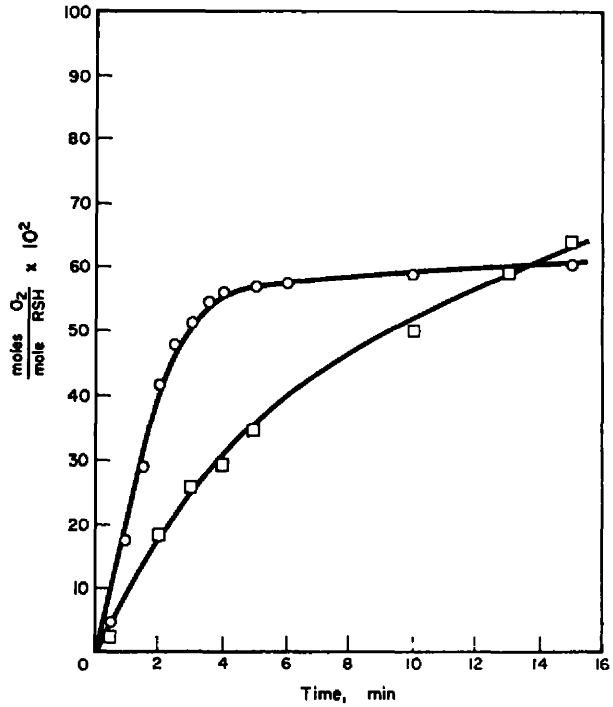

FIG. 5. Rates of oxygen consumption for $1\text{-}C_4H_9SH$ and C_6H_5SH in HMPA at 23·5°.
○ $1\text{-}C_4H_9SH$ in KOH/HMPA
□ C_6H_5SH in KOH/HMPA

The order of thiol anion reactivity (Fig. 5) observed, i.e., $1\text{-}C_4\overset{\ominus}{S} > C_6H_5\overset{\ominus}{S}$, is consistent with previous results in homogeneous media [9] in which it was observed that the most stable thiol anion undergoes electron transfer with oxygen least readily. The decreased rate of reaction and the low yield of acid obtained with 1-hexadecanethiol at 23·5° is apparently due to limited solubility of the thiol and disulphide at this

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[17] T. J. Wallace, J. E. Hofmann and A. Schriesheim, *J. Amer. Chem. Soc.* **85**, 2739 (1963).

temperature. At 80°, this problem is eliminated and a comparable rate of reaction and yield of acid is obtained. The brief study on the use of air as opposed to oxygen (Table 5) demonstrates that for laboratory scale purposes air can be employed as the oxidant in an open system if a continuous air flow is employed. Obviously, in a closed system the concentration of available oxygen at the surface is depleted with time and this accounts for the lower yield of acid obtained under these conditions

Some conclusions on the reactions of hydroxide and alkoxide bases with disulphides in these media can also be made. t-Butoxide ions appear to have a strong affinity for the alpha-[18] beta-[17] and benzylic-[15] carbon-hydrogen bonds of disulphide molecules while hydroxide ions preferrentially attack the disulphide linkage, i.e., they are more sulphur nucleophilic due to their decreased basicity.

EXPERIMENTAL

Reagents and starting compounds

Hexamethylphosphoramide (Monsanto Chemical Co.), dimethylformamide (Matheson, Coleman and Bell), pyridine (Matheson, Coleman and Bell) and tetramethylurea (Eastman Organic Chemicals) were distilled under N_2 over Linde-13X molecular sieves to remove any water that was present (10/1 vol ratio of solvent to sieve). The sieves had previously been conditioned by calcination under N_2 at 750° for 4 hr. All solvents were stored in a nitrogen dry-box equipped with a moisture conductivity cell.

Benzenethiol, 1-butanethiol, 2-methyl-2-propanethiol, *o*-toluenethiol, *p*-toluenethiol, 1-hexadecanethiol and 2,2-dipentyl-1-hexanethiol were obtained from either Aldrich Chemical Co. or Matheson, Coleman and Bell. The thiols were purified by distillation (under red. press. when necessary) through a 16-inch silvered column equipped with a tantalum-wire spiral. The physical properties of each thiol gave satisfactory agreement with those tabulated in Reid.[6] *o*-Carboxy-benzenethiol (m.p. 164°) was used without further purification.

Each disulphide was prepared according to the method described in Vogel.[19] One-tenth mole of each thiol was added to 50 ml of a 15% NaOH aq in a flask equipped with a stirrer and N_2 bubbler. Iodine (11·0 g) was added over a 2 hr period and each reaction mixture was then stirred overnight. *n*-Butyl disulphide (b.p. 87° at 10 mm) was purified by distillation through a 16-inch tantalum-wire spiraled column. Phenyl disulphide (m.p. 62°), *o*-tolyl disulphide (m.p. 38°) *p*-tolyl disulphide (m.p. 47°), *n*-hexadecyl disulphide (m.p. 55°) and 1-carboxyl-phenyl disulphide (m.p. dec.) were purified by recrystallization from alcohol. Yields based on purifier material varied from 65–85%. The physical properties of each disulphide were also in good agreement with those reported in the literature.[20]

Preparation of reaction mixtures and actual oxidation experiments

All base-solvent systems were made up to the appropriate molarity in a nitrogen dry-box. The alkali metal hydroxides were ground into powdered form before use. The desired thiol or disulphide was then added to the reaction flask which was sealed and transferred to the oxidation apparatus. In all cases, the solvent-base systems were heterogeneous.

The reaction flask was a heavy-walled Pyrex glass flask equipped with a ground glass sealed side-arm. The flask was attached to a water-cooled condenser which was attached to the source of O_2. The O_2 was stored in a polyethylene gas balloon under 1 atm. press. of O_2. The O_2 flowed from the balloon through a wet-test meter with 10 ml gradations and into a large drying-tube filled with indicating Drierite before entering the glass reaction vessel containing the reaction mixture. In actual operation, the system was initially purged with O_2 through the reaction flask side-arm, the side-arm sealed and an equilibrium press. was established. The reaction was then initiated by magnetic stirring at 1300 rpm. The volume of O_2 consumed as a function of time was determined from the wet-test meter which allows an estimation of the volume of gas consumed to within ±1 ml. With this method,

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[18] J. E. Hofmann, T. J. Wallace and A. Schriesheim, *J. Amer. Chem. Soc.* **86**, 1561 (1964).

[19] A. I. Vogel, *A Textbook of Practical Organic Chemistry* p. 498. Longman's Green, London (1959).

[20] E. E. Reid, *Organic Chemistry of Bivalent Sulphur Compounds* **111**, pp. 395–399. Chemical Publishing Co., New York, N.Y. (1960).

a constant O_2 partial press. of 1 atm. was maintained above the system. All reactions were allowed to proceed to completion, i.e., till no apparent O_2 consumption was observed. This oxidation technique and its applications have been described in detail previously.[21]

Quantitative analysis for reactants and products

Unreacted thiol was determined by potentiometric titration of a portion of the reaction mixture with standard $AgNO_3$ solution. Unreacted disulphide or disulphide produced as an oxidation product was determined by reduction of the disulphide to thiol in a Zn–acetic acid medium and subsequent titration with $AgNO_3$ as above. Hence, in the thiol oxidations

$$\text{mmole thiol (final)} - \text{mmole thiol (initial)} = \text{mmole thiol as } R_2S_2$$

Blank samples containing thiol, disulphide and a mixture of thiol and disulphide were subjected to these techniques and the results indicated that the method was essentially quantitative. Analyses for the acidic materials were carried out according to the method of Pobiner *et al.*[22] Two techniques can be employed. One involves an extraction-ion exchange-IR procedure and the other an extraction-UV procedure. Both rely on initial homogenization with water and subsequent extraction with cyclohexane to remove the starting material and nonacidic products. This removes any spectral interference in the determination of acidic products. The acidic products remain as their acid salts in the aqueous-dipolar solvent phase and are subsequently liberated by acidification with HCl aq. If the acid is aromatic, it can be quantitatively determined directly by UV spectroscopy from standard curves. If the acidic material is aliphatic or presents a weak UV absorption, it is determined by the ion exchange-IR method. This involves treating the aqueous phase with Amberlite LA-2 anion exchange resin. The free acid is extracted with CCl_4 and quantitatively determined by IR spectroscopy. These methods were accurate to within 95–99% for all products identified.

Other methods of identification

In addition to the UV and IR comparison to authentic samples further proof for the formation of sulphonic acids was obtained by the preparation of known derivatives of 1-butanesulphonic acid and benzenesulphonic acid. These acids were isolated by conventional methods from large-scale oxidation reactions. The phenyl hydrazinium salt of benzenesulphonic acid was prepared from an alcohol–ether solution and melted at 178–180° (reported m.p.[23] 179°). The anilinium salt of 1-butanesulphonic acid prepared in the same manner melted at 159–160° (reported m.p.[24] 159–160°).

[21] T. J. Wallace, W. Bartok and A. Schriesheim, *J. Chem. Educ.* **40**, 39 (1963).

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