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REACTIONS OF SODIUM SULPHIDE—I

WITH COMPOUNDS CONTAINING HYDROXYL GROUPS

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Abstract—Aqueous solutions of sodium sulphide (*ca* 10%) reagent were reacted at 250° with compounds containing OH groups. This work was part of a programme designed to test the usefulness of the Na_2S solution degradation technique for determining the primary structure of humic acids. The compounds reacted here and the principal products detected (shown in brackets) were: cinnamyl alcohol (benzyl alcohol, benzoic acid, 3-phenylpropan-1-ol, 3-phenylpropionic acid), benzyl alcohol (little reaction), 3-phenylpropan-1-ol (little reaction), 1,2-dihydroxy-1-phenylethane (phenylacetic acid, acetophenone, 1-phenylethanol), catechol and hydroquinone (recovered starting compounds + polymer products). Sodium hydroxide gave the same products with cinnamyl alcohol, but in different proportions. Possible mechanisms for these reactions are discussed.

INTRODUCTION

Sodium sulphide has been widely used in the wood pulping industry since 1870, when U.S. patents were granted for the delignification of wood with a mixture of Na_2S and NaOH.[1] Not surprisingly much of the model studies on the reactions of Na_2S with compounds containing the OH group have involved materials related to lignin monomer units. Unfortunately little quantitative data are available on the amounts of the degradation products produced, and the identification of these products has often involved a degree of speculation.

Our interest in degradation reactions with Na_2S arose from structural studies on humic acids.[2,3] These are the principal organic polymeric constituents of soils,[4] and they would appear to be the most abundant of the naturally occurring polymers. Their structures are relatively unknown, and progress in this area of research has been impeded by the lack of degradative reagents and techniques which give fragments that can be unambiguously assigned to structures in the polymers. Saturated solutions of Na_2S, under autoclave conditions at 250°, have yielded more than 60% by weight of ether-soluble products[2,3] from the natural polymers. Because many of these soluble products could arise by further degradation of monomeric units initially released from the humic acids, it is necessary to know how, and to what extent, such further degradations might take place under the reaction conditions. Comprehensive compilations of such data on degradation products could permit relevant gross structures to be assigned to the polymers when the compositions and amounts of the materials in the digests are known.

This paper will report the first of a series of studies designed to investigate the behaviour of components thought to be relevant in humic acid structures when reacted with Na_2S solutions. Attention will be focused here on compounds which contain the OH group.

Previous work[5] has shown that, when guaiacol (2-methoxyphenol) was treated with a 10% Na_2S solution at 251 ± 3°, cleavage of the ether linkage provided a maximum yield of catechol (*ca* 80%) after 1 hr, and that the amount of this product slowly decreased during subsequent heating. According to Enkvist and Turunen 1-hydroxycyclopentanecarboxylic acid was formed as a side reaction through the benzilic acid rearrangement of the cyclohexane-1-2-dione intermediate.

Heating veratryl alcohol (3,4-dimethoxybenzyl alcohol) with 10% Na_2S solution[5] was said to produce 4-hydroxy-3-methoxybenzyl alcohol, 3,4-dihydroxytoluene, and catechol. Although reaction mechanisms were not discussed it is probable that sulphur-containing intermediates were formed since vanillyl alcohol (4-hydroxy-3-methoxybenzyl alcohol) produced the sulphide in 77% yield when treated at 79–95° with a Na_2S solution.[6] Sulphides were reported not to be formed in the absence of the *para* OH group.

DISCUSSION

Results from reactions with Na_2S, or with NaOH, of cinnamyl alcohol (**1**), benzyl alcohol (**2**), 3-phenylpropan-1-ol (**3**), 3-phenylpropan-1-al (**4**), 1-

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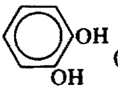
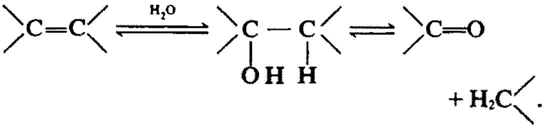
Table 1. Reactions of compounds with Na_2S

Experiment	Conditions	Starting material (g)	Products (g)
a	Na_2S, 250°	1. $PhCH{=}CH.CH_2OH$ (10·00)	$PhCH_2OH$ (2·78), $Ph(CH_2)_3OH$ (2·52) $PhCOOH$ (1·30), $Ph(CH_2)_2COOH$ (0·95)
b	NaOH, 152°	1. (0·500)	$PhCH_2OH$ (0·254), $Ph(CH_2)_3OH$ (0·056) $PhCOOH$ (0·013), $Ph(CH_2)_2COOH$ (0·037)
c	NaOD 143°	1. (0·500)	$PhCH_2OH$ (0·245), $PhCH_2CD_2CH_2OH$ (0·025) $PhCOOH$ (0·052), $PhCH_2CD_2COOH$ (0·026)
d	Na_2Sin D_2O 250°	1. (0·738)	$PhCH_2CD_2CH_2OH$ (0·019) $PhCH_2OH$ (0·440) + $PhCH{=}CHCH_2OH$ (0·191) Acids (0·008), not investigated.
e	Na_2S, 250°	2. $PhCH_2OH$ (10·00)	$PhCH_2OH$ (7·62), $PhCOOH$ (0·71)
f	Na_2S, 250°	3. $Ph(CH_2)_3OH$ (5·00)	$Ph(CH_2)_3OH$ (3·33), $Ph(CH_2)_2COOH$ (0·50)
g	NaOH, 153°	4. $PhCH_2CH_2CHO$ (0·500)	$Ph(CH_2)_2COOH$ (0·100) $Ph(CH_2)_3OH(x)$ $PhCH_2OH(y)$ (0·380) [x : y = 85 : 15] + polymer
h	Na_2S, 255°	5. $PhCHOHCH_2OH$ (3·00)	$PhCH_2COOH$ (0·70), $PhCOCH_3$ (0·71) $PhCHOHCH_3$ (0·71)
i	Na_2S, 250°	6.  (5·00)	6 (2·95) + polymer + possible cleavage products
j	Na_2S, 255°	7.  (3·00)	7 (1.12)

phenyl-1,2-ethanediol (5), catechol (6), and quinol (7) are summarised in Table 1.

Cinnamyl alcohol was chosen because it has some features of lignin monomer units thought to be precursors in humic acid biosynthesis.[7] In addition to the hydroxyl group of interest it contains a double bond which might be expected to undergo cleavage. It was essential, if the degradation technique were to be of value for humic acid studies, that the aromatic nucleus be stable under the experimental conditions. Separate experiments had indicated that high temperatures were necessary since little reactivity was observed at 130°.

The products from reaction of 1 under experimental conditions *a* (Table 1) could not be predicted by the hydrolytic cleavage mechanism of Shemyakin and Shchukina,[8] which was cited in earlier model studies.[5] According to this the addition of water across the double bond is followed by cleavage as follows



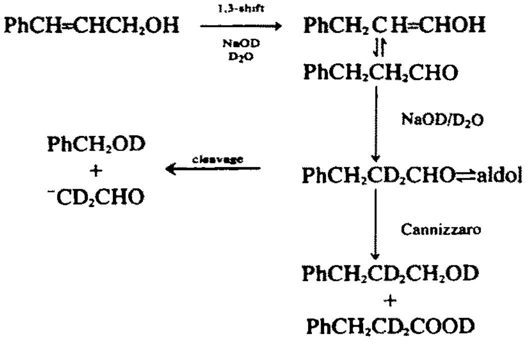


Fig 1.

When 1 was reacted with *ca* 19M NaOH (experiment *b*, Table 1) the identified products were the same as in experiment *a*, but the preportions were different. Reaction with sodium deuteroxide (experiment *c*, Table 1) produced $PhCH_2OH$, $PhCH_2CD_2CH_2OH$, $PhCOOH$, and $PhCH_2CD_2$-$COOH$. We illustrate in Fig 1, on the basis of the products from the reaction of 1 with NaOH and NaOD, our interpretation of the reaction mechanisms involved. An intramolecular mechanism, involving a 1,3-prototropic shift in the cinnemyl alcohol, is possible according to work by Cram.[9] The resulting enol would tautomerise to the keto-form, and deterium exchange would then take place to yield the α,α-dideutero aldehyde. This aldehyde could then undergo the reactions indicated (Fig 1) to give the products detected. Aldol condensation is expected, but this reaction is exothermic[10] and probably reversible. Thus the favoured products would be benzyl alcohol (the cleavage product) and $PhCH_2CD_2CH_2OD$ and $PhCH_2CD_2COOD$ (the Cannizzaro products in Fig 1). Some evidence for the occurrence of the Cannizzaro reaction with aldehydes containing α-hydrogen atoms is contained in a Geissman[11] review (for *iso*-butyraldehyde heated with a $Ba(OH)_2$ solution at 150°). The small amounts of benzoic acid found in experiments *b* and *c* (Table 1) were, presumably, formed by the oxidation of benzyl alcohol with alkali.[12]

Since the neutral components from the reaction of cinnamylalcohol with Na_2S in D_2O (experiment *d*, Table 1) had identical MS and NMR spectra to those from the reaction with NaOD we suggest that the the alkalinity of the Na_2S solution ($pH = 12{\cdot}7 \pm 0{\cdot}2$) was responsible for the first stage of its reaction with cinnamyl alcohol. Later reactions were modified by the sulphidity of the solution. Product differences in experiments *a* and *d* reflect different experimental conditions in the two instances.

Further evidence for the proposed mechanism in Fig 1 was obtained from the reaction of **4** (experiment *g*, Table 1) with concentrated base. The aldehyde (500 mg) yielded 3-phenyl-propionic acid (100 mg), plus a neutral fraction (380 mg) which contained 3-phenylpropan-1-ol and benzyl alcohol (in the ratio 85 : 15, respectively), and polymer. It seems, therefore, that **1**, under experimental conditions *c* and *d*, formed the aldehyde slowely *in situ*.

Any aldol polymer product formed would be rapidly produced as the solution warmed up and could be expected to be of high molecular weight. Complete depolymerisation was unlikly, but the fact that the Cannizzaro products together with the cleavage product were produced suggests that the mechanisms outlined in Fig 1 are feasible.

Benzyl alcohol was the predominant product in the reaction of **1** with Na_2S at 250°. Thus the degradibility of this product was studied in experiment *e* (Table 1). The products of the reaction showed that little alteration of starting material (92% recovery) had taken place. Some conversion by oxidation to benzoic acid occurred. There was no evidence for the types of reactions on veratryl alcohol observed by Enkvist and Turunen.[5] It is probable that the *para* OH group in this alcohol facilitated the formation of sulphur intermediates which decomposed to give the compounds claimed (Fig 2).

When 3-phenylpropan-1-ol was heated for 2 h with 10% Na_2S at 250° only 10% of the alcohol was oxidised to the acid (experiment *f*, Table 1). No cleavage of the aryl-alkyl bond could be detected. This is at variance with other results[5] which indicated that cleavage to yield benzene might be expected. Lack of such cleavage in the case of **3** (and also **2**) is important for humic acid studies where the ideal degradative agent should not produce extensive modifications in the degradation products.

A humic acid, as the result of periodate oxidation experiments by Murphy and Moore,[13] was thought to contain 15·6% by weight of glycol containing compounds. Experiment *h*, (Table 1) investigated the cleavage of **5**. The results in Fig 3 indicate that little cleavage had occurred, but that the glycol was transformed to an acid (**8**), ketone (**9**), and an alcohol (**10**). That cleavage did not take place agrees with the suggestion[8] that glycols undergo hydrolytic cleavage when the bond is sufficiently polarised by adjacent groups. The phenylacetic acid (**8**) might have arisen by a Willgerodt[14] mechanism since some of our work (unpublished) suggests that polysulphide moieties are involved in Na_2S reactions. This is supported by the report[15] that, under Willgerodt conditions, styrene oxide yielded phenylacetamide. The forma-

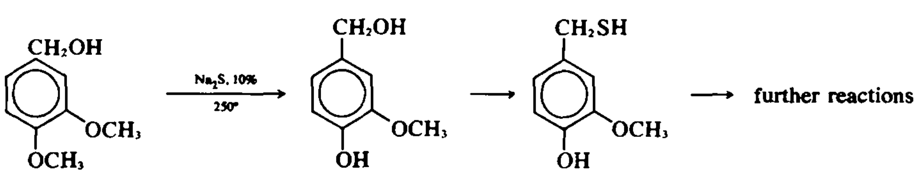


Fig 2.

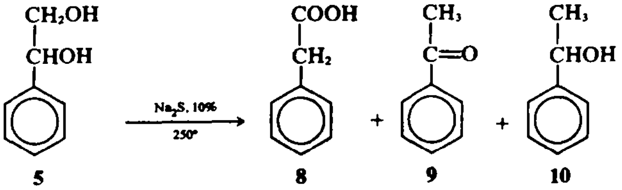


Fig 3.

tion of acetophenone (**9**) and 1-phenylethanol (**10**) cannot be explained with confidence. Possibly **9** could have formed by dehydration followed by tautomerisation, and **10** by reduction of the glycol or ketone. Reduction processes in alkaline conditions are not unknown and may involve hydride ion transfer.[16]

Catechol has been detected in Kraft mixtures[17] and also in several humic acid degradation mixtures.[18] Some theories on the biogenesis of humic acids propose that lignin products are involved as precursors. Thus the stability of **6** under reaction conditions *i* is important.

Catechol was recovered in 59% yield, but polymeric and possibly cleavage products were also present in the digest. The black polymer was presumably formed by phenolic coupling reactions[19] in the alkaline medium.

Quinol (**7**) was researched for the same reasons as **6**. Recovery of starting material (experiment *j*, Table 1) was 37%, and TLC of the reaction mixture suggested that the remainder was converted to polymer and possibly to cleavage products. It would appear, therefore, that it should be possible to detect any phenolic compounds liberated during the degradation of humic acids with Na_2S.

EXPERIMENTAL

Sodium sulphide solutions (*ca* 10%, 60 g $Na_2S.9H_2O$ in 160 cm^3 of distilled water) were freshly prepared for each experiment. Unless otherwise stated, experiments were conducted in air in a stainless steel rocking autoclave (1100 cm^3 capacity) at 40 to 50 atmospheres. For anaerobic autoclave and Carius tube (45 cm long, sealed volume = 95 cm^3) conditions, pure N_2 was bubbled through the contents, the containers were evacuated, then filled with N_2 and sealed. Reaction products, unless stated otherwise, were extracted with ether (volumes in parenthesis) at the pH of the digest (neutral fractions), or after acidification to pH 1 with 2M H_2SO_4 (acidic fractions), then dried with anhyd $MgSO_4$, and the ether removed at atmo pressure. Any sulphur which precipitated on acidification was removed by extracting the ether solubilized acids in base (2M NaOH, 3 × 25 cm^3), reacidifying, and again extracting with ether. TLC was carried out on silica gel (Kieselgel G nach Stahl). Spots were usually detected with iodine vapour, but in some instances UV fluorescence, diazotised *p*-nitroaniline, reduced methylene blue or potassium ferricyanide-ferric chloride reagent[20] were used. GLPC was conducted on a Pye 104 instrument with a flame ionization detector, and 5 ft × $\frac{1}{4}$ in and 15 ft or 30 ft × $\frac{3}{8}$ in columns [packed with polyethyleneglycol adipate (PEGA), 10%, and silicone oil SE-30, 10%, both on Universal Support, 60–85 mesh, from Phase Separations Ltd.] were used for analytical and for preparative separations, respectively. PEGA was used to separate neutral mixtures and SE-30 was used to separate the methyl esters of the acidic fraction. Column temp are given in parentheses.

Methyl esters for GLPC were prepared by adding 1 cm^3 of reagent [prepared by bubbling BF_3 gas into abs MEOH (25 cm^3) until the solon had increased in weight by *ca* 4 g, or by adding a few drops of BF_3-etherate (48% w/w BF_3) to Mg dried MeOH] to 5–10 mg of the acid or mixture of acidic compounds in a test tube, standing for 5 min over a boiling water bath, then adding water (10 cm^3) and extracting with ether. NMR spectra were recorded at 100 MHz on a Perkin-Elmer R14 instrument, and CCl_4 and DMSO-d6 were used as solvents for non-phenolic and for phenolic compounds, respectively. NMR data are not generally recorded in this paper since the spectra of all the compounds have been described before in the literature; we did, in fact, run spectra on pure authentic specimens of all the non-labelled compounds reported for the purpose of analysing the product mixtures. Mass spectra were determined on an AEI MS9 instrument.

Experiment a. Cinnamyl alcohol (**1**, 10·00 g) was autoclaved in 200 cm^3 of *ca* 10% Na_2S at 250° for 2 h after a 5 h warm-up period. No volatile compounds were collected after cooling. Neutral (ether, 3 × 100 cm^3) and acidic compounds (ether, 3 × 100 cm^3) amounted to 5·3 and 2·25 g, respectively. NMR and GLPC (170°) analyses, and comparisons with authentic samples, identified the products in Table 1.

Experiment b. **1** (0·500 g) was heated in a N_2 atmosphere (Carius tube) with 10 cm^3 of 19M NaOH for 13 h at 152°. Neutrals (ether, 5 × 10 cm^3) yielded 0·310 g of brown oil. Acidics (ether, 5 × 10 cm^3) were washed with 5% w/v $NaHCO_3$ solution (3 × 10 cm^3), and the aqueous extract, after acidification, was extracted with ether to yield 0·050 g of product. Results (NMR and GLPC) are shown in Table 1.

Experiment c. **1** (0·500 g) was heated in a nitrogen atmosphere (Carius tube) for 16 h at 143° with 10 g D_2O (isotopic purity ≥ 99·7 atom% D) to which 2·46 g of sodium metal had been added. Fractions, separated as for experiment *b*, consisted of 0·270 g of brown mobile liquid neutrals and 0·060 g of yellow acidic solids. NMR and preparative GLPC (PEGA, 150°, 30 ft column) identified the neutral products in Table 1. $PhCH_2CD_2CH_2OH$ was compared with the non-labelled compounds. Its NMR spectrum showed two proton singlets at 2·66 and at 3·67 ppm which is consistent with both D atoms in the C-2 position. Top mass values were 138 and 136, respectively, for the deuterated and non deutrated compounds. NMR of the acidic fraction suggested benzoic acid, plus an aromatic compound with a singlet at 2·87 ppm which suggested $PhCH_2CD_2COOH$ or $PhCHDCD_2COOH$. Methylation and preparative GLPC (SE-30, 180°, 15 ft column) gave compounds with top masses of 136, and 166, respectively (for $PhCO_2CH_3$ and $PhCH_2CH_2CO_2CH_3$).

Experiment d. **1** (0·738 g) was heated at 250° for 13 h with 0·866 g of anhydrous Na_2S ($Na_2S.9H_2O$ was dehydrated during 28 days over phosphoric oxide in a vacuum desiccator) in 3·722 g D_2O in a 50 cm^3 capacity autoclave. The neutral products (0·650 g of brown liquid) isolated and identified [NMR, GLPC (PEGA, 150°)] are listed in Table 1. Acidics (0·008 g) were not studied further.

Experiments e and f. The conditions used for the digestion of benzyl alcohol (**2**, experiment *e*) and 3-phenylpropan-1-ol (**3**, experiment *f*) were the same as for experiment *a*, except that half quantities were used in the case of *f*. Products and yields are given in Table 1.

Experiment g. 3-Phenylpropan-1-al (**4**) was digested for 15 h at 153° under the conditions reported for experiment *b*.

Experiment h. 1-Phenyl-1,2-ethanediol (**5**, 3·00 g) in 100 cm^3 of *ca* 10% Na_2S soln was autoclaved at 255° for 2 h after a 6 h warm-up. Preparative GLPC (160°, 30 ft column) of the neutrals separated acetophenone and phenylmethyl carbinol (Table 1), identified by NMR and IR. Esterification and GLPC (SE-30, 180°) showed the acidic fraction to be phenylacetic acid (Table 1) with a trace of benzoic acid (2%).

Experiment i. Catechol (**6**, 5·00 g) in 100 cm^3 of *ca* 10% Na_2S was autoclaved in an atmosphere of N_2 at 250° for 2 h after a 5 h warm-up. Acidics (3·38 g, continuous ether extraction for 48 h) were separated with 5% w/v $NaCHO_3$ into "phenolics" (2·95 g) shown (NMR) to be **6**, and a black polymer-like tar (0·30 g) which was not aromatic (NMR), and indicated by TLC to be a complex mixture with R_f values not greater than that for catechol ($R_f = 0·61$). No neutrals were isolated.

Experiment j. Hydroquinone (**7**, 3·00 g) in 100 cm^3 of *ca* 10% Na_2S solution was autoclaved in an atmosphere of N_2 at 255° for 2 h after a 3 h warm-up. After acidification to pH 1, ether extraction (8 × 30 cm^3) and removal of sulphur, 2·05 g of brown crystalline product, indicated by NMR to be mainly hydropquinone (purity = *ca* 55%), was isolated. TLC (benzene: acetone = 3 ; 1) showed a major component corresponding to hydroquinone ($R_f = 0·68$) which gave a colour reaction with diazotised *p*-nitroaniline. Faint traces were observed (iodine) above and below this spot. Benzequinone, which gives a blue colour with methylene blue, was not detected.

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