polar factors are proportional to the steric and polar factors involved in the dissociation of alcohols. For convenience, it is useful to consider substituents with positive values of $\phi$ as electron sinks and negative values as electron sources, since it can be assumed that for small molecules the polar effects would be more important than the steric effects. Similarly, we can tentatively assign the same meaning to $m$ as Hammett's $\rho$, namely that a positive $m$ would indicate that low electron density favors the reaction, while a negative $m$ would imply that the reaction is favored by high electron density. However, it should be recognized that if steric factors predominate in a reaction, the above is not necessarily true.

## Discussion

Figure 2 demonstrates the excellent correlations that are obtained using the substituent constants given in Table II, and Table III lists reaction series that were tested, together with their results. The standard deviation and correlation coefficients are excellent and bear out the validity of the model.[11] Reactions 20 and 21 are included in Table III to show that reactions other than ester hydrolysis would appear to follow this model.

Inspection of the slopes for the various reactions reported in Table III leads to some interesting speculations. For example, reactions 3, 6, 9, and 19 are for the alkaline hydrolysis of acetate esters in a variety of acetone–water mixtures. The change in slope that is observed for these reactions would appear to be related to the polarity of the solvent, the largest slope being in 70% acetone–water and the smallest slope in pure water. That this is quantitatively due to a polar effect rather than a special solvent effect in these reactions was established by plotting the slopes against Kosower's $Z$ values[12] and obtaining a linear relationship, the equation for the line being[13] $m = -0.0258Z + 2.935$.

The signs for the slopes for acid- and base-catalyzed hydrolysis of acetate esters (reactions 6 and 7) are both positive, but their absolute values are different, the acid reaction $m$ being a smaller positive number. This qualitatively accords with the expectation that alkaline hydrolysis is hindered by high electron density, while acid hydrolysis is aided. The involvement of steric effects in $\phi$ probably accounts for the failure of $m$ to be negative for acid-catalyzed reactions.

It is apparent that alcohol dissociation serves as an excellent model for solvolysis of aliphatic esters where substitution is in the alkyl portion of the molecule.

**Acknowledgment.**—The authors express their appreciation to Professors Kenneth A. Connors and Pasupati Mukerjee for helpful discussions and suggestions, and to Mrs. Lloyd Matheson and Dr. Paul Kramer for computer assistance. The support for computer time granted through the Research Committee of the University of Wisconsin is gratefully acknowledged.

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[11] Note that since dissociation constants of alcohols quantitatively parallel rates of reaction, we now have a fairly reliable estimate of dissociation constants for a number of alcohols which have not been experimentally studied, simply by interpolation from a plot of p$K_a$ *vs.* $\phi$.

[12] E. M. Kosower, *J. Amer. Chem. Soc.*, **80**, 3253 (1958).

[13] $Z$ values for 37% and 62% acetone–water mixtures were found by interpolation to be 88.5 and 84.8, respectively.

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# Aralkyl Hydrodisulfides.[1] X. Reactions with Iron Salts

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Redox reactions of hydroperoxides with ferrous or cuprous ion already have been elucidated.[2,3] Hydrodisulfides, thio analogs of hydroperoxides, however, may be expected to behave differently toward redox reagents in view of the information presented so far. For instance, aralkyl hydrodisulfides are oxidized to the corresponding diaralkyl tetrasulfides almost quantitatively with iodine,[4] 2,2-diphenyl-1-picrylhydrazyl, or benzoquinone,[5] and in the case of mercaptans which are considered the lower homologs of hydrodisulfides, they are oxidized with ferric ion in the presence of oxygen[6] or with ferric caprilate.[7] In the present Note we will report the reaction of aralkyl hydrodisulfides with iron salts.

Benzyl or benzhydryl hydrodisulfide in dioxane was added dropwise to an aqueous or a dioxane solution of ferric chloride hexahydrate at room temperature under a nitrogen gas stream. In both cases the color of ferric ion disappeared completely after the addition of an equimolar amount of the hydrodisulfide. The corresponding tetrasulfide was produced in good yields, as shown in experiments 1–3, Table I. A nearly equivalent amount of ferrous ion was formed in experiments 1–3, and an appreciable amount of proton was detected in experiments 1 and 2, where the determinations were successfully carried out by utilizing the aqueous layer. In Table I all the data were adjusted in per mole bases. Although each separated amount of tetrasulfide shown in experiments 1–3 was not quantitative, the reaction appeared to be a good one, because nmr spectra of the filtrate after the first recrystallization of the tetrasulfide indicated that the filtrate contained minor amounts of the disulfide and trisulfide along with the major component, the tetrasulfide. From the results shown in experiments 1–3, the main reaction path will be formulated as

$$2\mathrm{RSSH} + 2\mathrm{Fe}^{3+} \longrightarrow \mathrm{RSSSSR} + 2\mathrm{Fe}^{2+} + 2\mathrm{H}^{+} \quad (1)$$

Two possible side reactions were checked. The first possibility is a participation of a trace amount of oxygen which might have been present in the solution. Under atmospheric oxygen, the reaction was completed instantaneously by the addition of the first drop of aqueous ferric chloride solution, giving the result shown in experiment 4, Table I. This result, as compared with those in experiments 1–3, clearly indicates that ferric ion in the presence of a sufficient amount

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[1] Part IX: J. Tsurugi, T. Horii, T. Nakabayashi, and S. Kawamura, *J. Org. Chem.*, **33**, 4133 (1968).

[2] M. Kharasch, A. Fono, W. Nudenberg, and B. Bishof, *J. Org. Chem.*, **17**, 207 (1952).

[3] J. Kochi, *J. Amer. Chem. Soc.*, **84**, 3271 (1962).

[4] J. Tsurugi and T. Nakabayashi, *J. Org. Chem.*, **24**, 807 (1959).

[5] T. Nakabayashi and J. Tsurugi, *ibid.*, **28**, 813 (1963).

[6] E. E. Reid, "Organic Chemistry of Bivalent Sulfur," Vol. 1, Chemical Publishing Co., New York, N. Y., 1958, p 118.

[7] T. Wallace, *J. Org. Chem.*, **31**, 3071 (1966).

TABLE I

REACTIONS OF ARALKYL HYDRODISULFIDES (1 MOL) IN DIOXANE WITH AQUEOUS SOLUTIONS OF VARIOUS SALTS AT ROOM TEMPERATURE

| | Reactant system | | | | Products, mol or g-ion | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Expt | R in RSSH | Salt | Molar ratio of salt/RSSH | Oxygen | $H_2S$ | $RS_nR$ | Average value of $n$ | RSH | $Fe^{2+}$ | $H^+$ | Unchanged RSSH |
| 1 | $C_6H_5CH_2$ | $FeCl_3$ | 1 | Trace | 0.002 | 0.37 | 4 | 0 | 0.95 | 1.0 | |
| 2 | $(C_6H_5)_2CH$ | $FeCl_3$ | 1 | Trace | 0 | 0.42 | 4 | 0 | 0.92 | 0.85 | |
| 3 | $(C_6H_5)_2CH$ | $FeCl_3$[a] | 1 | Trace | 0 | 0.43 | 4 | 0 | 0.84 | ... | |
| 4 | $C_6H_5CH_2$ | $FeCl_3$ | 1:100 | Under atmospheric $O_2$ | 0.25 | 0.36 | 3.2 | 0.27 | | | |
| 5 | $C_6H_5CH_2$ | $FeSO_4$ | 1 | Trace | 0.37 | 0.30 | 2.89 | 0.25 | | | |
| 6 | $C_6H_5CH_2$ | $FeSO_4$ | 1:200 | Trace | 0.41 | 0.33 | 2.86 | 0.22 | | | |
| 7 | $(C_6H_5)_2CH$ | $FeSO_4$ | 1 | Trace | 0.28 | 0.32 | 3.71 | 0.34 | | | |
| 8 | $C_6H_5CH_2$ | $K_2SO_4$ | 1:200 | Trace | 0.46 | 0.44 | 2.75 | 0.03 | | | |
| 9 | $C_6H_5CH_2$ | KCl | 1:200 | Trace | 0.44 | 0.43 | 2.47 | 0.07 | | | |
| 10 | $C_6H_5CH_2$ | KI | 1:200 | Trace | 0.36 | 0.39 | 2.62 | 0.16 | | | |
| 11 | $(C_6H_5)_2CH$ | KCl | 1:200 | Trace | 0.28 | 0.34 | 3.67 | 0.32 | | | |
| 12 | $C_6H_5CH_2$ | None | | Trace | 0.46 | 0.51 | 3.15 | 0 | | | 0 |
| 13 | $(C_6H_5)_2CH$ | None | | Trace | 0.18 | 0.19 | 4.39 | 0.44 | | | 0.13 |
| 14 | $C_6H_5CH_2$ | None[b] | | Trace | 0.26 | 0.36 | 3.45 | 0.10 | | | 0.22 |
| 15 | $(C_6H_5)_2CH$ | None[b] | | Trace | 0 | 0 | | 0 | | | 1.00 |

[a] Dissolved in dioxane. [b] Dioxane alone.

of oxygen decomposed hydrodisulfide by a different path from eq 1. Thus, the reaction of the hydrodisulfide with ferric ion was not appreciably disturbed by possible presence of a trace of oxygen. The second possible side reaction would be the reaction of hydrodisulfide with ferrous ion produced in eq 1. In experiments 5–7 are shown the reaction products of the hydrodisulfides with ferrous sulfate, which is conveniently used as a pure source of ferrous ion. This reaction proceeded much more slowly than the one with ferric ion. Judging from evolution of hydrogen sulfide, it required 20 hr or longer for completion. The product distribution in experiments 5–7 rather resembles that in experiment 4 and differs remarkably from that in experiments 1–3. This difference, together with the slower rate with ferrous ion, suggests that the reaction with ferric ion was not disturbed with ferrous ion.

As shown in experiment 6, even a small amount of ferrous ion was sufficient to complete this kind of reaction. In this respect, we clearly recognize the difference between the reactions with hydroperoxides, which consume over a half molar amount of ferrous ion,[8] and those with hydrodisulfides. Since the ferrous ion did not reduce hydrodisulfides as in the case of hydroperoxides, it seems necessary to check the effect of other salts, such as potassium salts, which do not participate in redox reaction. The reactions with these salts were also slow, as were those with ferrous sulfate (20 hr or longer). The results are indicated in experiments 8–11. The product distribution from benzyl hydrodisulfide (experiments 8–10) differs considerably from that with ferrous sulfate (experiments 5–6), whereas that from benzhydryl hydrodisulfide with potassium chloride (experiment 11) is quite similar to that with ferrous sulfate (experiment 7), although this similarity may be incidental. From these results alone, it is not possible to decide whether the decomposition of hydrodisulfides is caused by ferrous sulfate or by other salts. In addition, there still remains a possibility that water or dioxane used as a solvent could be responsible for the decomposition of hydrodisulfides. To check this possibility, the decomposition reactions were attempted in a water–dioxane mixture containing no salt and in dioxane alone, and the results are indicated in experiments 12–15. The results in experiments 12 and 13 are similar to those with salts, and contrast with those in experiments 14 and 15. The net contributions of ferrous sulfate and other salts to the decomposition of hydrodisulfide in eq 1 remains obscure and, if any, may be minor.

As a summary, the reaction of hydrodisulfides with ferric ion in the absence of oxygen proceeds by eq 1. The disturbance by ferrous ion which is produced in eq 1 appears not to be serious. The redox behavior of the hydrodisulfides showed a clear contrast to that of hydroperoxides. The former behaves as a reductant, which is easily and almost quantitatively oxidized with ferric ion, while the latter is an oxidant, as is well known, in the reaction with ferrous ion.

### Experimental Section

Benzyl hydrodisulfide and benzhydryl hydrodisulfide were prepared by the method reported elsewhere.[4] Inorganic salts were commercial chemicals of high purity and were used as received. Commercial dioxane (CP grade) was refluxed over sodium and distilled before use. Melting points are uncorrected. Dibenzyl tetrasulfide and dibenzhydryl tetrasulfide were identified by mixture melting points with authentic samples. Nmr spectra were taken on a JNM 3H-60 spectrometer with tetramethylsilane as an internal standard. The amount of hydrogen sulfide was determined by the method reported elsewhere.[1]

**Procedure for the Reaction with Ferric Chloride.**—In a three-necked flask equipped with an equilibrated dropping funnel, a magnetic stirrer, and nitrogen inlet and outlet tubes, the latter of which was connected with absorbing bottles of hydrogen sulfide, was placed a solution of 5.4 g (20 mmol) of ferric chloride hexahydrate in 10 ml of water. The atmosphere was replaced by nitrogen. A solution of 3.13 g (20 mmol) of benzyl hydrodisulfide or 4.65 g (20 mmol) of benzhydryl hydrodisulfide in 40 ml of dioxane, which was bubbled with nitrogen in advance, was added, with stirring, to the ferric chloride solution for 20 min under continuous nitrogen bubbling at room temperature. Then the reaction mixture was extracted with benzene. The solvent was removed *in vacuo* from the dried extract to give oil which

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(8) A. V. Tobolsky and R. B. Mesrobian, "Organic Peroxides," Interscience Publishers, New York, N. Y., 1954, p 100.

could be induced to solidify by cooling for benzyl hydrodisulfide, or to give solid for benzhydryl series. Recrystallization of each solid from alcohol gave pale yellow crystals, 2.3 g (74%), of dibenzyl tetrasulfide, mp 52.5-53°, and 3.9 g (84%) of dibenzhydryl tetrasulfide, mp 82.5-83°. The amount of ferrous ion formed and the pH change in the reaction of benzyl hydrodisulfide or benzhydryl hydrodisulfide were determined as follows. (Data for the latter are shown in parentheses.) By using an aliquot of the aqueous layer, ferrous ion was analyzed colorimetrically by *o*-phenanthroline, indicating that the amount was 19 mg-ion (18.5 mg-ion). The remaining aqueous layer was diluted with water to 200 ml (100 ml). The pH of the solution was 1.20 (0.42). Before the reaction, the corresponding pH was 1.65 (1.06). This pH difference was found by titration to correspond to *ca.* 20 mmol (17 mmol) of sodium hydroxide, *i.e.*, *ca.* 20 mg-ion (17 mg-ion) of proton.

For experiment 3, 2.7 g (10 mmol) of powdered ferric chloride hexahydrate in 20 ml of dioxane was added to a solution of 2.3 g (10 mmol) of benzhydryl hydrodisulfide in 20 ml of dioxane and the mixture was stirred under a nitrogen atmosphere. At once the solution became pale yellow and a precipitate was formed. The precipitate (ferrous salt, 8.4 mmol) and the remaining organic solution (86% of dibenzhydryl tetrasulfide) were treated in a manner similar to that mentioned above.

For experiment 4, atmospheric oxygen was bubbled into the benzyl hydrodisulfide solution in the flask described above. Only one drop ($2 \times 10^{-4}$ mol or 0.01 mol/1 mol of hydrodisulfide) of the solution of ferric chloride hexahydrate from the dropping funnel was added. Vigorous evolution of hydrogen sulfide was observed. Since it appeared that hydrogen sulfide was coming out sparingly after effervescence ceased, the bubbling was continued for 2 days. (Hydrogen sulfide was not swept out smoothly, probably because the reaction mixture was not so acidic as in the case mentioned above.) The amount of hydrogen sulfide was determined, and then the reaction mixture was extracted with benzene. To an aliquot of the dried extract was added an excess of 0.1 $N$ ethanolic iodine solution. The amount of thiol was determined by titrating the solution with 0.1 $N$ aqueous sodium thiosulfate. Analytical procedure for polysulfides in the remaining benzene extract was identical with that reported elsewhere.[9]

**Procedure for the Reaction with Ferrous Sulfate or Other Inorganic Salts.**—In the same apparatus as mentioned above, equimolar or 0.005 $M$ ferrous sulfate in 10 ml of water was added to a stirred solution of 10 mmol of hydrodisulfide in 30 ml of dioxane under nitrogen atmosphere at room temperature. Hydrogen sulfide evolved slowly for *ca.* 24 hr. The hydrogen sulfide was analyzed and the reaction mixture was extracted with benzene. The amount of thiol was determined by using an aliquot of the benzene extract, and the remainder was oxidized with ethanolic iodine solution. The excess of iodine was removed by washing with aqueous sodium thiosulfate solution followed by water, and was dried. The solvent was evaporated *in vacuo* and yellow viscous oil was obtained. The quantity of polysulfides in the oil was determined by using nmr spectra with 1,1,2,2-tetrachloroethane as another internal standard for integral purpose only. [CH peaks for authentic dibenzhydryl di-, tri-, tetra-, and pentasulfides were $\tau$ 5.27, 4.79, 4.45, and 4.40, respectively (s, 7 w/w in $CCl_4$).]

The reaction of hydrodisulfide with inorganic salts was carried out in the same way as described above. Long periods (20 hr or more) were required to complete each reaction, judging from the evolution of hydrogen sulfide.

**Procedure for the Decomposition of Hydrodisulfides in Dioxane-Water or Dioxane Alone.**—To a stirred solution of 1.5 g (9.5 mmol) of benzyl hydrodisulfide or 1.2 g (5.2 mmol) of benzhydryl hydrodisulfide in 30 ml of dioxane was added 10 ml of water under nitrogen atmosphere at room temperature. After 24 hr, the dioxane and water were removed *in vacuo*. Yellow oil obtained was subjected to nmr analysis, by which the amounts of thiol,[1] polysulfide,[1] and remaining hydrodisulfide [$C_6H_5CH_2SSH$, $\tau$ 7.26; $(C_6H_5)_2CHSSH$, $\tau$ 7.28 (both s, 7 w/w in $CCl_4$)] were estimated. Experiments with dioxane alone were run similarly to that described above.

**Registry No.**—Dibenzyl tetrasulfide, 4816-54-0; dibenzhydryl tetrasulfide, 21367-78-2.

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[9] S. Kawamura, Y. Otsuji, T. Nakabayashi, T. Kitao, and J. Tsurugi, *J. Org. Chem.*, **30**, 2711 (1965).

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# Chemistry of 4-Pyridineglyoxylonitrile Oxime and Methyl 4-Pyridineglyoxylate Oxime Ethers

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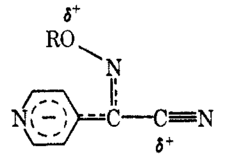
An investigation was made of the reaction of 4-pyridineglyoxylonitrile oxime O-methyl (and benzyl) ethers (**3** and **4**) with hydroxide. Reaction of both **3** and **4** with methanolic potassium hydroxide occurred readily to give the corresponding amides **7** and **8**. Hydrolysis of the methiodide of **4** (**11**) also led to the formation of amide **12** (Scheme I). Compounds **9**, **10**, and **13**, which are geometrical isomers of **8**, **7**, and **12**, were prepared from methyl 4-pyridineglyoxylate oxime (**2**) as illustrated in Scheme I. Isomerization of **8** to **9** was achieved by using sulfuric acid. Synthetic details are given in the Experimental Section.

**Electrophilic Character of the Oximino Carbon.**—Our finding that the nitrile group in **3**, **4**, and **11** is attacked preferentially to the oximino carbon was interesting. The marked stability of the oximino carbon to attack by hydroxide was illustrated through an experiment in which both **8** and **9** were recovered unchanged after being refluxed in methanolic potassium hydroxide. If attack by hydroxide had occurred, then isomerization would have been evident. The apparent low electrophilic character of the oximino carbon (relative to that of the nitrile carbon) can be rationalized on the basis of a distribution of electron density throughout the conjugated system as represented in structure A. Inductive effects (structure B), which would increase the electrophilicity of the oximino carbon, must be less important. Nevertheless, it is expected that compounds such as $\alpha$-hydroxy-$\alpha$-(O-alkyl)hydroxylamino-4-pyridineacetonitriles (C) if formed would be stable enough for isolation because of the strong electron-withdrawing influence of both the cyano and the 4-pyridyl moieties. Analogy can be drawn from the previous isolation of carbinolamine intermediates in the formation of pyridinium aldoximes



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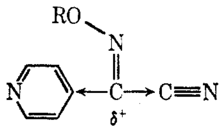

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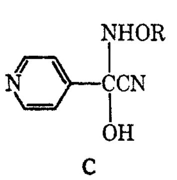

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[1] Taken in part from the Ph.D. thesis of B. C. T., University of Delaware, June 1969.

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