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Formamidinesulfinic Acid as a Reducing Agent. I.

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Formamidinesulfinic acid, namely thiourea dioxide, was synthesized for the first time by Banett,[1] oxidizing thiourea by 6% neutral hydrogen peroxide under ice cooling. The pure formamidinesulfinic acid decomposes at 129~130°, evolving sulfur dioxide.[2] In general, formamidinesulfinic acid is known to be a reducing agent,[3] capable of reducing many kinds of metallic ions to metals in the presence of ammonia; for example Cu^{2+} is reduced to Cu metal and Sn^{4+} to Sn metal, also Cd^{2+}, Ni^{2+}, Co^{2+}, Ag^{+} and Sb^{5+} are reduced to the corresponding metals.

On the other hand, concerning the reduction of organic compounds by this substance, only one brief report by Gore[4] was found, who reported that aromatic nitro, azoxy, azo, and hydrazo compounds were reduced to amines, quinones to hydoquinones, and dyes to leuco-dyes using this agent. However the methods used and results obtained were not described in detail.

Therefore, we planned to study the utilizability of this substance for the reduction of many kinds of organic compounds. For the first step of this study, the reduction of aliphatic and aromatic disulfides to the corresponding thiols is reported in this paper. The reduction to the thiols was carried out in the most cases of the disulfides with satisfactory yields.

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Experimental Method

The reduction is carried out by adding disulfides to the solution of formamidinesulfinic acid in the presence of caustic alkali, using water, ethanol, pyridine, dimethylformamide, dioxane, or their mixture as the solvent, and keeping the mixture at 70~80° on a water bath with stirring for 3~5 hours.

After the reduction is over, the solvent is removed and the residue consisting of alkali salt of thiol is dissolved in water or in some cases, without removing the solvent the reaction mixture is poured into water, then filtering the insoluble substance off, the aqueous solution of the sodium salt of thiol is rendered acidic with dil. HCl, and thiol is separated and purified in proper way.

Results and Discussion

In these reductions, as the results of the experiments, it was found that the yields of the thiols were strongly affected by the solvents used and the molar ratio of the disulfides, alkali, and formamidinesulfinic acid.

As the example of aliphatic disulfide, we took diethyl disulfide and dibenzyl disulfide and as the aromatic disulfide, bis(*p*-chlorophenyl) disulfide, bis(*p*-tolyl) disulfide, and dithiosalicylic acid. The results are shown in Table I.

As for the solvent, ethanol was found to be the best in all cases and for the quantity of the alkali added, in general, the yield of the thiols decreased remarkably when the molar ratio of disulfides to that of the alkali was 1 to 2. On the other hand,

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1) B. Banett : J. Chem. Soc., **97**, 63(1915).

2) R. Kitamura : J. Pharm. Soc. Japan, **58**, 818(1938).

3) J. Böseken : Rec. trav. chim., **55**, 1040(1936).

4) P.H. Gore : Chemistry & Industry, **1954**, 1355.

TABLE I.

Disulfide (1 mole)	Solvent	Formamidinesulfinic acid (mole)	Alkali (mole)	Yield (%)
Diethyl	A	1/2	2	45
Diethyl	A	1	4	66
Dibenzyl	A	1	4	81
Dibenzyl	A	2	8	75
Di-*p*-tolyl	A	1	4	68
Di-*p*-tolyl	A	1	2	33
Di-*p*-tolyl	W	1	4	—
Di-*p*-tolyl	P	1	4	trace
Di-*p*-tolyl	DF	1	4	56
Di-*p*-chlorophenyl	A	1	4	79
Dithiosalicylic acid	A	1	4	—
Dithiosalicylic acid	DF	1	4	—
Dithiosalicylic acid	P	1	4	trace
Dithiosalicylic acid	P	2	8	—
Dithiosalicylic acid (Na salt)	W	1	4	—

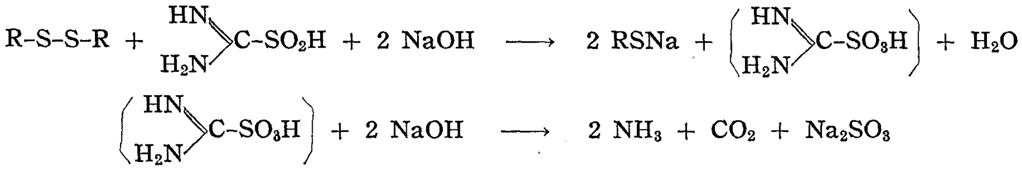
Solvent : A : ethanol
W : water
P : pyridine
DF : dimethylformamide

in the case of the 1 to 4 ratio, the yields of the thiols were found to be satisfactory.

Concerning the mole of formamidinesulfinic acid, in our experiments, 1 mole of formamidinesulfinic acid was found to be enough to reduce 1 mole of disulfide and even when more reducing agent was used, the yield of the thiols was nearly the same as when 1 mole of formamidinesulfinic acid was used. As shown in Table I, dithiosalicylic acid could not be reduced by the above-mentioned method.

In the course of the procedures, the violent evolution of ammonia was observed and that of sulfur dioxide was also observed when the reaction mixture was acidified after the reaction was over.

Considering these results, that is moles of formamidinesulfinic acid and alkali required and also the evolution of ammonia and sulfur dioxide, this reaction is presumed to be in the following way, through formamidinesulfonic acid as an intermediate. Formamidinesulfonic acid could not be isolated.



$$R\text{-}S\text{-}S\text{-}R + \begin{matrix}HN\\H_2N\end{matrix}\!>\!C\text{-}SO_2H + 2\ NaOH \longrightarrow 2\ RSNa + \left(\begin{matrix}HN\\H_2N\end{matrix}\!>\!C\text{-}SO_3H\right) + H_2O$$

$$\left(\begin{matrix}HN\\H_2N\end{matrix}\!>\!C\text{-}SO_3H\right) + 2\ NaOH \longrightarrow 2\ NH_3 + CO_2 + Na_2SO_3$$

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