

**XLV.—The Development of Colour by Photochemical Change in Concentrated Solutions of Ammonium Thiocyanate.**

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LIESEGANG (Eder's *Jahrb. Photographie*, 1894, 49) showed that the colour developed when concentrated aqueous solutions of ammonium thiocyanate are exposed to light is not due to traces of iron, and Holmes (J., 1926, 1690) attributed it to colloidal sulphur produced in the irreversible change  $\text{NH}_4\text{SCN} \longrightarrow \text{NH}_4\text{CN} + \text{S}$ . Werner and Bailey (*ibid.*, p. 2970), however, dissented from this view and suggested that the cause might be found in some tautomeric form of thiocyanic acid or in the formation of a coloured complex between thiocyanic acid and the solvent. Bhatnagar and others (*J. Indian Chem. Soc.*, 1927, 4, 229) concluded that the colour was due to cyanogen sulphide and that the precipitate was a polymeride  $(\text{CNS})_x$ , suggesting the mechanism  $\text{NH}_4\text{CNS} + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4\text{OH} + \text{HCNS}$ ,  $2\text{HCNS} + \text{O} \longrightarrow \text{H}_2\text{O} + 2\text{CNS}$ ,  $x(\text{CNS}) \longrightarrow (\text{CNS})_x$ . Montignie (*Bull. Soc. chim.*, 1928, 43, 106) and Patten and Smith (*Trans. Roy. Soc. Canada*, 1928, 22, III, 221) considered ferric thiocyanate to be responsible for the colour. According to Montignie, the reaction  $2\text{FeSO}_4 + \text{O} + 6\text{HCNS} \rightleftharpoons \text{H}_2\text{O} + 2\text{H}_2\text{SO}_4 + 2\text{Fe}(\text{CNS})_3$  occurs.

The work now described (finished before the last two papers were available) was initiated in view of the conflicting nature of the foregoing conclusions.

EXPERIMENTAL.

1. Samples of ammonium thiocyanate which did not give rise to the colour on insolation were produced (i) by the action of either ammonium carbonate or ammonium sulphate on barium thiocyanate, prepared by treating ammonium thiocyanate with baryta, and also (ii) by boiling a fairly dilute solution of the salt with animal charcoal, boiled with pure hydrochloric acid and dried before use. Moreover, these samples did not develop colour when treated with pure hydrochloric acid, hydrogen peroxide, or chlorine.

2. Iron was detected in the salt by arc and spark spectral lines.

3. Traces of iron (as ferrous or ferric salt or as metal) added to the pure samples produced a colour upon insolation.

4. Both the intensity of the colour developed and the time required for its disappearance in the dark were proportional to the amount of iron introduced.

5. The ethereal extract of the colour developed with ferrous salt and ammonium thiocyanate was intensified by dilution.

6. A solution in water-free pyridine exhibited a photochemical change similar to that in aqueous solution.

7. Even after repeated insolutions and storage in the dark, aqueous solutions yielded no precipitate.

8. Gelatin inhibited the development of the colour.

*Discussion.*—Expts. 1, 2, and 3 show that traces of iron present as impurity are responsible for the coloration. Expt. 4 rules out the possibility that the iron functions as a catalyst, and shows that it actually takes part in the formation of the coloured compound, light supplying the energy. The formation of ferric thiocyanate is doubtful, for it is decolorised neither by heating (Scott, "Standard Methods of Analysis," 4th edtn., 1927, 246) nor by keeping in the dark (Dhar, *J. Indian Chem. Soc.*, 1929, 6, 143); moreover, it is bleached by light, and is entirely extracted by ether, the extract leaving a coloured residue on evaporation, whereas the extract from the insolated solutions does not behave so. The photochemical colour, produced with traces of ferric iron insufficient to show coloration ordinarily, can hardly be due to ferric thiocyanate (compare *J. Soc. Chem. Ind.*, 1929, 48, 336T). Expt. 5 distinguishes the colour developed with ferrous iron from that of ferric thiocyanate. Expt. 6 shows that the colour is probably not dependent upon hydrolysis or upon oxygen-containing solvents. The photochemical change in Expt. 7 appears to be reversible. The ready disappearance of the colour in the dark, on heating, or on dilution, its non-appearance in the absence of oxygen and traces of iron, and its appearance at high concentrations show that the compound is a sort of loose additive complex of ferrous thiocyanate with oxygen, and that its formation is probably connected with the changes at high concentrations.

Further work on the subject is in progress.

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