CCXXI.—*The Action of Light on Concentrated Aqueous Solutions of Ammonium Thiocyanate.*

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ACCORDING to Liesegang (Eder's *Jahrb. Photographie*, 1894, 49), concentrated aqueous solutions of ammonium thiocyanate (and also of other thiocyanates, including aluminium), if exposed to sunlight for 1 minute, turn bright red, the colour disappearing in the dark after 2 minutes. He could reproduce this behaviour indefinitely with the same solution, but was unable to ascribe a cause to it, remarking that it could not be due to the presence of a trace of iron, as the blood-red thiocyanate is itself bleached by light in presence of a reducing agent. The phenomena appeared of interest and, on the suggestion of Professor Allmand, the author undertook their further investigation, in the hope that they might prove capable of quantitative treatment. The work was carried out in the winter of 1923—24, and consequently artificial light sources were employed. Preliminary results only were obtained, but it is believed that they are worthy of the following brief record.

(*a*) Freshly-prepared concentrated solutions of ammonium thiocyanate, contained in glass vessels, were insolated by the full light of the quartz–mercury lamp. In the course of 5 to 15 minutes—depending on the concentration of the solution and the distance of the lamp—a pink to red coloration developed in the solution. It never became bright red, however, even on prolonged insolation. Traces of some gas were given off (not collected or analysed) and it was noted that, with the strongest solutions, this gas appeared before the colour change commenced. On placing the solution in the dark, the colour slowly faded, taking at least 15 minutes for complete disappearance, the period required increasing with the length of the previous insolation. On re-exposure to light, the colour returned, as described by Liesegang. No chemical change could be detected in the solution.

(*b*) When insolated in quartz vessels under the same conditions, the slow development of colour after the first few minutes was noted as before. It did not, however, become so intense as when in glass. Instead of this, continued exposure resulted in the deposition of a white or slightly yellow solid on the side of the vessel next the source of light. This clearly shut off the active rays, for its formation rapidly ceased. At the same time, the pink colour began to fade, and the liquid became cloudy. When now the flask was rotated so as to expose a fresh surface, more solid was deposited, and in this way the whole of the walls of the vessel in contact with the solution became ultimately covered with the solid. Visible colour had before this completely disappeared. The contents of the flask were then extracted with sulphur-free benzene, in which ammonium thiocyanate is insoluble. The solid dissolved with difficulty. On evaporation of the benzene extract, a small residue was obtained which gave strong tests for sulphur, but not for nitrogen, whilst the aqueous solution was found to contain traces of cyanide and of a reducing agent (sulphite or nitrite ?). A sulphuric–chromic acid mixture removed the deposit from the walls of the vessel only after several weeks' contact.

(*c*) On one of the few favourable days, a concentrated solution (in glass) was exposed to sunlight. The colour appeared rapidly, as reported by Liesegang. It was still, however, only a pink, not a bright red, and its disappearance in the dark was still slow.

(*d*) Other artificial light sources were used—tungsten, carbon, and iron arcs. These gave results of the same nature, but in view of the varying quantities of energy consumed, nothing can be said as to whether one source of light is specifically more effective in its action than another. Certainly, the iron arc appeared to give a slightly deeper colour. In addition, after prolonged exposure, exceeding 40 hours, in a *glass* vessel, to the radiation of the iron arc, a slight precipitate was noticed.

(*e*) The more concentrated the solution, the more marked was the coloration. No colour was observed with solutions weaker than $4N$, although traces of a deposit could be detected on prolonged insolation.

(*f*) In order to show the usual effects, the solutions must apparently be freshly made. Even the most concentrated solutions, if stored in the dark for some days, show but little change after several hours' exposure.

(*g*) On the other hand, the presence of air (oxygen?) seems to play a part. A freshly-prepared solution was divided into two portions. One was stored in the dark for 5 days; the other was freed from air at room temperature by periodically putting the vessel containing it into communication for a few seconds with a space evacuated to 10^{-4} mm., and containing a train of calcium chloride and phosphorus pentoxide tubes. On subsequent insolation, the evacuated solution showed no trace of any coloration, however long the exposure ,whilst the unevacuated solution behaved normally—the development of colour was slow, owing to storage. A partly evacuated solution (made up only two days previously) at first turned pink, but then became colourless, remained so, and developed a trace of a precipitate.

(*h*) On the hypothesis that the development of colour and its disappearance might possibly be due to the reversible change

$$NH_4CNS \underset{\text{Dark}}{\overset{\text{Light}}{\rightleftarrows}} NH_4CN + S \text{ (colloidal)},$$

comparative insolations were carried out with solutions of composition $10N$-NH_4CNS and $10N$-$NH_4CNS + N$-KCN. The addition of the potassium cyanide was found to delay very markedly the appearance of the colour. On the other hand, if a few drops of potassium cyanide were added to an insolated (pink) solution, the colour immediately disappeared, being replaced by a faint yellow tinge. If the solution were then allowed to stand for a week or so, a small amount of a yellow precipitate was seen to have been deposited. This again gave the tests for sulphur, but not for nitrogen.

(*k*) A few experiments made with an ultra-condenser type of ultra-microscopic apparatus gave indefinite results, owing to the rapid adsorption of the solid phase on the quartz walls of the cell interfering with the observations. The only information of interest obtained was that, whereas a solution made up with specially prepared water, carefully filtered and kept in the dark, was optically clear, large numbers of very fine *microscopic* particles immediately appeared on exposing it to ultraviolet light, the insolation not being long enough for any colour to develop. The solution was actually examined with a Wratten K-3 filter interposed between the mirror of the microscope and the ultra-condenser, the filter being removed and replaced between the two observations. No change could thus take place during examination.

It would be premature at this stage to attempt any detailed explanation of these complex phenomena. Apart, however, from the other chemical changes detected (formation of a reducing agent and evolution of a gas) it is suggested as a working hypothesis that the absorption of long-wave ultra-violet light (passed by glass) causes the *irreversible* photo-reaction $NH_4CNS \longrightarrow NH_4CN + S$ (as sol); that the insoluble sulphur forms aggregates of sub-microscopic size which are responsible for the pink colour; that these submicrons can slowly unite to form particles of microscopic size which are colourless or practically so (the spontaneous fading of the colour); and that this process of coagulation is accelerated by addition of potassium cyanide or by ultra-violet light of shorter wave-length (passed by quartz). The actual extent of decomposition is very slight, and in dilute solutions negligible. (Compare Volhard, *Annalen*, 1877, **190**, 1—61.)

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