benzene (both ideal cases, in terms of the theory discussed) have been prepared, and show no indications of polar characteristics for the halogens present.

2. A possible mechanism for the elimination of positive halogen from amino derivatives, involving the formation of a quinoidal intermediate compound and subsequent 1,3 elimination, has been suggested.

3. It is pointed out that failure to react under given conditions is no adequate indication of polar structure.

4. The assumption of negativity and positivity, respectively, for certain halogens attached to carbon in the benzene ring, is shown to rest on essentially the same basis.

Chicago, Illinois

[Contribution from the Research Laboratory of the Eastman Kodak Company, No. 303]

ADDITION COMPOUNDS OF ALLYLTHIO-UREA WITH SILVER HALIDES[1]

By S. E. Sheppard and H. Hudson

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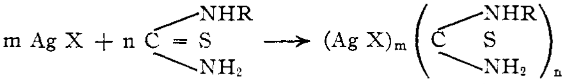
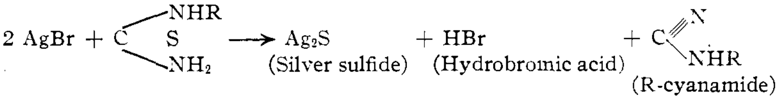
In an investigation on photographic gelatin[2] it was found that the photographic activity of certain gelatins depends upon the presence of traces of mustard oil, or allyl isothiocyanate, and the thio-urea (allyl thiocarbamide, thiosinamine) derived therefrom. Further, it was shown that this photographic sensitizing power was a general property of thioureas and a number of cognate bodies,[2] being due to the formation of small traces of silver sulfide in the silver halide grains. These traces of silver sulfide were considered to constitute the so-called "sensitivity centers" of photographic theory.

The chemical reactions in this sensitizing process are essentially



$$m\,\mathrm{Ag\,X} + n\,\mathrm{C}\overset{\mathrm{NHR}}{\underset{\mathrm{NH_2}}{=\mathrm{S}}} \longrightarrow (\mathrm{Ag\,X})_m\left(\mathrm{C}\overset{\mathrm{NHR}}{\underset{\mathrm{NH_2}}{\mathrm{S}}}\right)_n \qquad (1)$$

(where m and n are simple integers)



$$2\,\mathrm{AgBr} + \mathrm{C}\overset{\mathrm{NHR}}{\underset{\mathrm{NH_2}}{\mathrm{S}}} \longrightarrow \underset{\text{(Silver sulfide)}}{\mathrm{Ag_2S}} + \underset{\text{(Hydrobromic acid)}}{\mathrm{HBr}} + \underset{\text{(R-cyanamide)}}{\mathrm{C}\overset{\equiv\mathrm{N}}{\underset{\mathrm{NHR}}{}}} \qquad (2)$$

In Reaction 2 sufficient alkalinity is necessary to neutralize the hydrobromic acid and the cyanamide.

The present investigation is concerned with the formation and properties of the intermediate double compounds of silver halide and thio-

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[1] Read in part at the Regional Meeting of the American Chemical Society, January, 1926.

[2] Sheppard, *Phot. J.*, 65, 380 (1925).

urea, indicated in Reaction 1. So far not very much information has been found in the literature concerning such compounds. Reynolds[3] described a definite crystalline compound of silver bromide with thiourea, $(CSN_2H_4)_2.AgBr$, obtained by the interaction of silver nitrate with $(CSN_2H_5)_4NBr$ in equimolecular proportions. He further stated that analogous compounds had been obtained with other silver salts, and later described these.[4] With silver nitrate, the general result was the identification of the compounds $(CSN_2H_4)_3.AgNO_3$ and $(CSN_2H_4).AgNO_3$, while some evidence of the existence of the intermediate substance, $(CSN_2H_4)_2.AgNO_3$, was obtained.

Coming to the silver halides, he found that *silver bromide* forms two compounds with thio-urea, $(CSN_2H_4)_2AgBr$ and $CSN_2H_4.AgBr$. With *silver chloride* he obtained only the 2:1 compound, with no evidence for the 1:1 compound, and with *silver iodide* only the 1:1 compound. It may be noted that while Reynolds obtained only a 2:1 compound with silver cyanide, and states that "as with silver chloride, a 1:1 compound has not been obtained," Rosenheim and Loewenstamm[5] obtained by digestion of freshly precipitated silver cyanide in aqueous thio-urea white, glistening scales of a 1:1 compound, which they describe as "extraordinarily unstable, separating silver sulfide again on recrystallization."

When we turn to the substituted thio-ureas, the previous indications are much more meager. We have not yet had access to a dissertation by Falke[6] which contains some previous work on compounds of the metal salts with thiosinamine (allyl thiocarbamide). In this a 1:1 compound with silver chloride is mentioned, occurring in "white, feathery needles."

Silver Chloride and Thiosinamine.—The compound was prepared by mixing equimolecular quantities of allyl thiocarbamide, potassium chloride and silver nitrate, each at 0.1 *M* concentration. A microcrystalline precipitate is at once formed which was filtered off and washed free from soluble salts. Analysis of this gave sulfur and silver chloride corresponding to the 1:1 compound, $NH_2.C(=S)NHC_3H_5.AgCl$. Solubility measurements were made on this by percolating the powder with

TABLE I

SOLUBILITY OF $NH_2.CS.NHC_3H_5.AgCl$

Temp., °C.	Subs. per liter, g.	Subs. per liter, g. moles $\times 10^4$
15	0.0517	2.0
25	.0816	3.1
35	.1313	5.0
50	.4578	17.6

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[3] Reynolds, *J. Chem. Soc.*, **53**, 857 (1888).

[4] Reynolds, *ibid.*, **61**, 249 (1892).

[5] Rosenheim and Loewenstamm, *Z. anorg. Chem.*, **34**, 62 (1903).

[6] Falke, Dissertation, Marburg, **1893** *Beilstein*, **4**, 210 (1922).

distilled water at various temperatures, until saturation values were reached on analysis of the supernatant liquid.

Silver Bromide and Thiosinamine.—For the preparation of the 1:1 compound, a quantity of well-washed silver bromide was fused in a porcelain crucible. Two glass rods were allowed to freeze in the melt, and served as supports after the crucible was broken away. The fused mass was cleaned by immersion in sodium thiosulfate solution and water, and then suspended in an aqueous solution of allyl thiocarbamide (thiosinamine), one part in 1000 parts of water. Bunches of small, needle-shaped crystals developed on the surface of the silver bromide overnight (Fig. 1). A quantity of crystals were grown in this manner, washed with distilled water and dried over sulfuric acid. Analysis was made of the silver content by digestion with ammonium sulfide, the silver sulfide formed being filtered off, dried and weighed. A sample analysis follows.

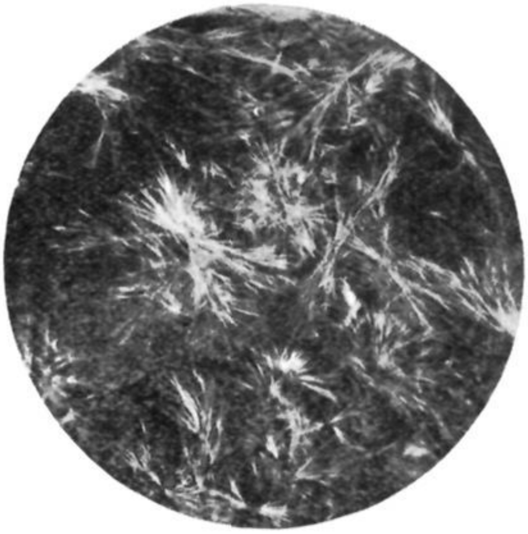


Fig. 1.—Crystals of allyl thiocarbamide—silver bromide. Magnification eight times.

Anal. Subs., 0.1534: Ag_2S calcd. for $AgBr.C_4N_2H_8S$, 0.0626. Ag: calcd., 35.50. Found: 35.51.

Control analyses of the nitrogen by Kjeldahl's method confirmed this, corresponding to 97.4% of that calculated for $AgBr.C_4N_2H_8S$. This compound corresponds, therefore, to the 1:1 compound of silver bromide and thio-urea, described by Reynolds, and the 1:1 compound of silver chloride and thiosinamine, ascribed to Falke.

Solubility measurements were made on the 1:1 silver bromide compound at 15, 25, 35 and 50°. A quantity of the compound was put in known volumes of water and shaken for 48 hours in a thermostat kept constant to 0.1°, and the amount dissolved determined by conversion to silver sulfide. The values obtained are given in Table II.

TABLE II

SOLUBILITY OF $C_4N_2H_8S.AgBr$

Temp., °C.	Subs. per liter, g.	Subs. per liter, g. moles × 10^4
15.0	0.0446	1.46
25.0	.071	2.33
35.0	.120	3.94
50.0	.293	9.63

Silver Iodide and Thiosinamine.—Although there was evidently an action of dilute thiosinamine solution upon fused silver iodide, it was not found possible to grow crystals in the same way as with silver bromide. An attempt to prepare the 1:1 compound was made as follows.

Eleven and six-tenths g. of allyl thiocarbamide and 16.6 g. of potassium iodide were dissolved in 500 cc. of water. To this there was slowly added with stirring 17.0 g. of silver nitrate in water. A voluminous precipitate formed which settled to the bottom, consolidating to a sticky, plastic mass. The supernatant liquor gave no reaction for silver sulfide when heated with ammonia. From this it appears that the 1:1 compound is formed, and that its solubility at room temperature is of the order of silver iodide or silver sulfide.

The solid decomposes very readily, giving silver sulfide, so that it appears that the following reaction had gone to completion: $AgNO_3 + C_4N_2H_8S + KI = AgI.C_4N_2H_8S + KNO_3$. The compound was difficult to isolate in a pure state because it formed a glassy mass instead of crystallizing. It appears, however, somewhat soluble in alcohol from which it may be precipitated in a semi-colloidal state by the addition of water.

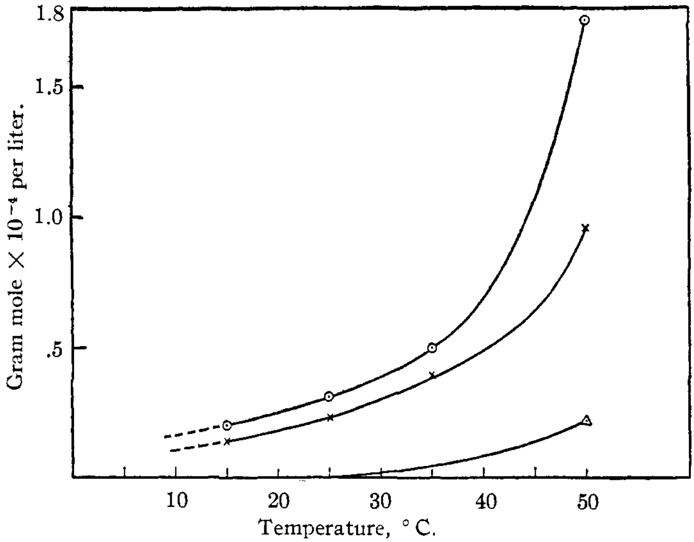


Fig. 2.—Solubility of silver halide-allyl thiocarbamide compound in water. ⊙, silver chloride; ×, silver bromide; △, silver iodide.

A solubility determination was made at 50° with the result given in Table III.

Table III

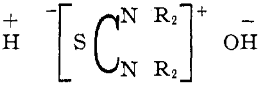
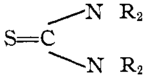
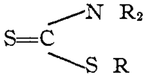
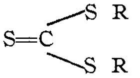
Temp., °C.	Subs. per liter, g.	Subs. per liter, g. moles
25		ca. 2.5×10^{-7}
50	0.0778	2.21×10^{-4}

Effect of Soluble Halides.—Preliminary measurements have shown that excess of the soluble halides reduces the solubility of the double compounds in water. This effect is being studied, as well as the influence of excess of soluble halides and other salts on the formation of the double compounds and on their decomposition.

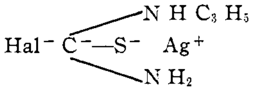
Composition and Constitution.—On comparing our observations with those of previous observers, we may note that although in several of our experiments considerable excess of allyl thiocarbamide was used over the 1:1 molecular ratio of silver halide:allyl thiocarbamide, and up to 1 mole of silver halide to 2 moles of allyl thiocarbamide, no evidence of other double compounds, for example, 1Ag Br:$2C_4H_8N_2S$, was obtained, but only of solutions. It is possible, therefore, that the 1:2 compound of allyl thiocarbamide is more difficult to isolate than that of thiocarbamide itself, and this is being investigated.

The compounds of thio-ureas with metal salts have been considered from the point of view of the Werner coördination theory by Rosenheim and Loewenstamm.[5] The mode of combination of the silver halide will depend upon the constitution assigned to the thio-ureas. Lecher and co-workers[7] in an important memoir on the "Constitution of Thiourea and the Thiourea Salts" give strong evidence for the ampholytic character of thio-urea, according to the following general scheme.

R = H or alkyl

Bases	Anhydrobases		Remarks
		Normal thio-urea	Strong bases and strong acids (Hybrid ions and therefore apparently very weak bases)
		Dithio-urethan	No bases
		Ester of trithiocarbonic acid	No bases

On this conception, the 1:1 double compounds would have the constitution



The contiguity of the silver ion and the negative sulfur atom agrees with the ready formation of silver sulfide.

Relation to Photographic Sensitizing.—The isolation and observed solubilities of these double compounds have important bearings on photographic sensitization, which will be discussed elsewhere. It may be suggested, however, that the much lower solubility of the silver iodide compound, compared with that of the 1:1 silver bromide compound, make it an important intermediate in the process.

It is known not only that silver iodide in small amounts (less than 3%) considerably influences photographic sensitivity, but also that in certain

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[7] Lecher and co-workers, *Ann.*, **445**, 35 (1925).

high-speed emulsions the proportion of iodide is greater in the larger than in the smaller grains.[8] Further, it has been shown by Sheppard, Wightman and Trivelli[9] and by Clark[10] that the larger grains resist desensitizing more than the small ones. This may be due to the silver sulfide nuclei being larger or more firmly "rooted," and protected by silver iodide rather than silver bromide, in the larger grains.

Summary

1. The literature on the double compounds of thio-ureas with silver salts is briefly reviewed.

2. The preparation of the 1:1 compounds of allylthio-urea with silver chloride, silver bromide and silver iodide is described.

3. Solubility measurements are given for the temperature range 15 to 50°.

4. The constitution of these double compounds is discussed and their relation of photographic sensitizing.

ROCHESTER, NEW YORK

[CONTRIBUTION FROM THE DIVISION OF PLANT NUTRITION, UNIVERSITY OF CALIFORNIA]

PHOTOSYNTHESIS WITH MALACHITE GREEN

BY DEAN BURK

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According to Baly, Heilbron and Barker[1] and Baly,[2] "an aqueous solution of malachite green saturated with carbon dioxide yields formaldehyde on exposure to light behind a thick plate glass screen. In the absence of carbon dioxide no formaldehyde is produced." No details of technique in support of this claim were offered. Baur and Büchi[3] repeated the experiment, but they were unable to conclude that the formaldehyde came from the carbon dioxide. Indeed there was no doubt, from their experiments, that the presence of carbon dioxide in the exposed solutions of malachite green, the concentrations of which varied eight-fold, from 15 to 125 parts per million, reduced the yield of formaldehyde. When the absence of all carbonate or bicarbonate ions was insured by the addition of varying amounts of barium hydroxide, the yields of formaldehyde were increased decidedly, even though the solutions may have been partially or entirely discolored before exposure was made, owing to the alkalinity. The fact that the colorless solutions, when

[8] Renwick, Baldsiefen and Sease, *Phot. J.*, **66**, 163 (1926).

[9] Sheppard, Wightman and Trivelli, *Trans. Faraday Soc.*, **19**, 296 (1923).

[10] Clark, *Phot. J.*, **64**, 91 (1924).

[1] Baly, Heilbron and Barker, *J. Chem. Soc.*, **119**, 1032 (1921).

[2] Baly, *Rec. trav. chim.*, **41**, 528 (1922).

[3] Baur and Büchi, *Helv. Chim. Acta*, **6**, 959 (1923).