

# Participation of Gelatin Aminogroups In Silver Halide Emulsions Sensitization with Organothio Compounds

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## Abstract

There was delivered a comparative study of chemical sensitization of AgBr emulsions by various classes of organosulfur compounds. It was established that the activity of a sensitizer is defined predominantly by the rate of nucleophilic substitution of sulfur. In water solutions of amines and gelatin the mainstream process of nucleophilic substitution of sulfur is aminolysis. The rate of hydrolysis of compounds under study is negligibly small in comparison with that of the process mentioned above. Hence the amino groups of gelatin take part in the process of sulfide sensitization.

## Introduction

It is known<sup>1</sup> that in the course of chemical ripening light sensitivity of AgHal microcrystals increases due to the formation of impurity centers on their surfaces. Sheppard was the first to take notice of the sensitizing action of sulfur-containing compounds in 1925. He showed that in the presence of such compounds, silver sulfide formed on the surface of AgHal microcrystal which acted as an impurity center. Before<sup>2</sup>, in studying the interrelation of structure and sensitizing action of sulfur-containing organic and organophosphorous compounds in the process of chemical ripening, it was shown that the thiol form of the compounds involved was more active than thion one. This was probably due to a faster hydrolysis of thiol derivatives resulting in the formation of sulfide anion. The hydrolysis of organo-sulfur compounds is an example of nucleophilic sulfur substitution. Bearing in mind that during chemical ripening both chemical sensitizer and adsorbed gelatin can be found on the microcrystal surface one might suggest the participation of gelatin aminogroups in the process of nucleophilic sulfur substitution in the organo-sulfur sensitizer. At the same time, taking account of the higher amine nucleophilic reactivity as compared with water, one could expect the preferred sulfur substitution in the reaction between an organo-sulfur compound and gelatin aminogroups.

## Results and Discussion

We undertook a systematic study of the nucleophilic sulfur substitution in organo-sulfur compounds in the course of their reaction with water and aqueous amine solutions. Taken as a simplest sulfur-containing chemical sensitizer was thioacetamide. The comparison of thioacetamide and thiourea sensitizing activities shows that the effectiveness of thioacetamide at the stage of model bromo-iodo-silver emulsion ripening is much higher than that of thiourea, which is in contrast with the data available in literature suggesting that thioamides of carboxylic acids, thioacetanilide in particular,<sup>1</sup> are not chemical sensitizers. Thus, at 60° C maximum light sensitivity of the emulsion is reached in 45 min in the presence of  $4.00 \cdot 10^{-3}$  mol/g.-at.Ag of thiourea and  $1.17 \cdot 10^{-5}$  mol/g.-at.Ag of thioacetamide.

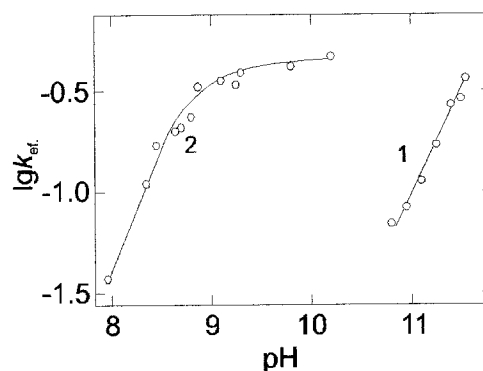


Figure 1. The pH dependence of thioacetamide hydrolysis (1) and aminolysis with benzilamine (2) rate. Aqueous solution, 80 °C.

This difference in the effectiveness of the sensitizers involved results from much higher speed of thioacetamide hydrolysis. Its hydrolysis proceeded at 80° C at measurable speed over the pH range ~11-11.5 (Figure 1). Under the same conditions thiourea practically does not hydrolyze. A noticeable thiourea hydrolysis occurs only at a higher temperature or in more alkaline media. Thus, it has been shown that the effectiveness of sulfur sensitizer depends directly on the rate of its hydrolysis with the forming of sulfide anion.

The rate of hydrolysis was determined by the increase in the concentration of the sulfide anions. This increase can be described by an ordinary first-order equation, which made it possible to calculate the first-order rate constants ( $k_{ef}$ ). Given in Figure 1 is the pH dependence of the thioacetamide hydrolysis rate. From Figure 1 it is seen that  $\lg k_{ef}$  - pH plot is linear, with the slope 0.98. This indicates that the thioacetamide hydrolysis is a second-order reaction:

$$\omega = \frac{d[S^{2-}]}{d\tau} = k \cdot [TAA][OH^-] = k_{ef} \cdot [TAA]$$

where [TAA] is the concentration of the thioacetamide. As expected, the rate of sulfide anions releasing during the thioacetamide hydrolysis increases greatly in the presence of amines. The investigation of the kinetics of this reaction in aqueous benylamine solutions showed the increase in the reaction rate with the increasing pH. Assuming that the reaction with benzylamine, like that with hydroxide anion, is a second-order reaction being the first order faith regard both to thioacetamide and unprotonated amine form:

$$\omega = k \cdot [TAA][C_6H_5CH_2NH_2],$$

the relationship between the observed and real second-order rate constant will take the form:

$$k_{ef} = k / (1 + a_{H^+} / K_{BH^+}).$$

This is completely confirmed by the pH dependence of  $\lg k_{ef}$  shown in Figure 1. Thus, thioacetamide aminolysis giving a corresponding amidine represents, in this case, a slow stage of the sulfide anion formation:

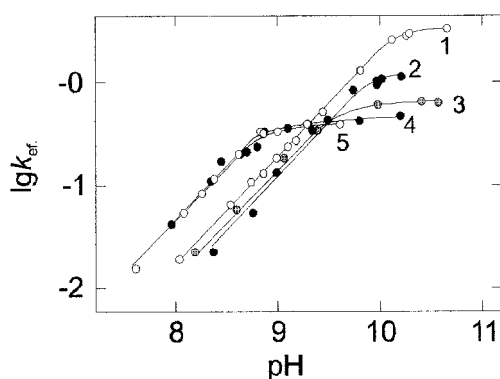
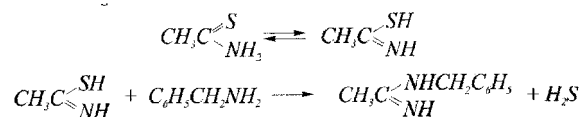


Figure 2. The pH dependence of thioacetamide aminolysis rate for the reaction with *n*-butylamine (1), 2-aminopropionic acid (2) aminoacetic acid (3) benzylamine (4) and allylamine (5) Aqueous solution 80 °C.

The relation between the structure of primary amines and their reactivity in the above reaction was established by comparing the rate constants for the reaction of thioacetamide with the amines of different basicities (Figure 2). It was found that nucleophilic reactivity of primary amines increased with their basicity. For this reason in the medium with pH~1 in which all amines are practically unprotonated the rate of the reaction with thioacetamide increases with increasing basicity in the order: benzylamine allylamine < aminoacetic acid < 2aminopropionic acid < *n*-butylamine. In more acid medium where amines are protonated practically completely, the relationship between reactivities and basicities is reversed. The investigation of the thioacetamide reaction with secondary and tertiary amines revealed the kinetic features (Figure 3) identical with those observed for primary amines. It should be noted that tertiary amines of the same basicity with primary amines (e.g. butylamine with  $pK_{BH^+}$  10.61 and triethylamine with  $pK_{BH^+}$  10.67) are less reactive due to the steric hindrance.

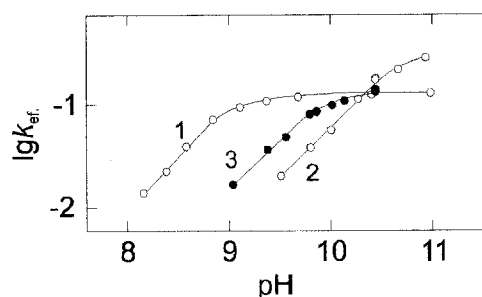


Figure 3. The pH dependence of thioacetamide aminolysis rate for the reaction with morpholine (1) diethylamine (2) triethylamine (3). Aqueous solution 80 °C.

Thus, the comparison of the reaction rates for the sulfur nucleophilic substitution in hydrolysis and in the course aminolysis confirms the higher nucleophilic reactivity of amines and, hence, of gelatin amino-groups.

The very first results obtained from studying the ripening AgBr emulsions in the presence and in the absence of gelatin confirmed completely the suggestion about the active participation of gelatin amino-groups in the process of chemical sensitization by organo-sulfur sensitizers.

## References

1. S.E. Sheppard, *Photogr. J.*, 1925. v. **65**, p.380.
2. Zavlin P. M. Diaconov A.N., Kuznelsov L.I. et al. *Zh.N.i P.F.*, 1996. v. **41**. p.66.