On the Reactions Between Some Organic Sulfur Compounds and Silver Ions with Potentiometric Titrations

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Introduction

Reactions between organic photographic fog-inhibitors and silver ions were measured by means of silver potentiometric titration in this laboratory. The senior authors, Kikuchi and Sakaguchi reported those on the pyrimidine derivatives[1,2,3] and Kikuchi, Sakaguchi, and Murobushi on the benzimidazoles and rhodanines[4]. The present report intends to clarify the reactions between some organic compounds other than cited before and the silver ion by the same method with an improved device. The substances chosen in this report are as follows:

potassium thiocyanate (I)
thiourea (II)
thiosemicarbazide (III)
benzaldehyde thiosemicarbazone (IV)
piperonal thiosemicarbazone (V)
p-dimetylamino benzaldehyde thiosemicarbazone (VI)
p-acetamide benzaldehyde thiosemicarbazone (VII)
o-nitrobanzaldehyde thiosemicarbazone (VIII)
m-nitrobenzaldehyde thiosemicarbazone (IX)
p-nitrobenzaldehyde thiosemicarbazone (X)
phenyl thiosemicarbazide (XI)
benzaldehyde phenyl thiosemicarbazone (XII)

Some other substance not containing sulfur

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* Y. Sakaguchi has been in Fuji Photo. Film Co., since April, 1952.

1) S. Kikuchi and Y. Sakaguchi, *Journ. Sci. Phot. Japan* (in Japanese) **12**, No. 4, 3-7 (1950); abstracted in *Sci. et industr. Phot.*, **23** (2) 307 (1952).

2) Y. Sakaguchi and S. Kikuchi, ibid., **13** No. 4, 126-131 (1951); abstracted in *Sci. et industr. Phot.*, **23** (2) 178(1952).

3) S. Kikuchi and Y. Sakaguchi, *Sci. et Industr. Phot.*, **23A** 248-260 (1952).

4) S. Kikuchi, Y. Sakaguchi and K. Murobushi, *Bull. Soc. Scient. Photo. Japan* (in English), No. 2, 10-19 (1952).

are also chosen:

hydrazine (XIII)
urea (XIV)
guanidine (XV)
diphenyl guanidine (XVI)

These sulfur compounds are mainly chain compounds and some of these are apparently photographic sensitizers or even fogging agents. The authors wished to know the effect of the substitution of amino group of thiourea in connection of this reaction.

Experimental Part

(a) Pen-recording System of Potential—The silver potential of substances is measured potentiometrically. The voltage difference of a cell which is set up with the calomel and the silver electrode is amplified and read on a pen-writing recorder described in the previous paper[3,5]

(b) Automatic Titrator[5] — The addition of silver nitrate solution to the reagent is done with the automatic titrator designed in this laboratory (Fig. I). A syringe plunger is driven by the system of synchronous motor, gears, belt, and travelling nut. The change of gears enables four steps of the travelling nut's speed (50, 10, 2.5, and 0.625 mm/min.). Besides changes of the connection of belt and pulley make seven stages which are 2, 1.5, 1.25, 1 (standard), 0.75, 0.625, and 0.5. The nut's speed should be changed in 28 steps between 100–0.3125 mm/min. But the combinations of gears and belt make two pairs of the same speed, so 26 steps in total are interchangeable. The size of the syringe may be changeable from 1 to 10 cc also. The present experiment took place under conditions of about 5 cc. syringe and 1.25 mm/min. speed which corresponded to 0.67 cc./5 min.

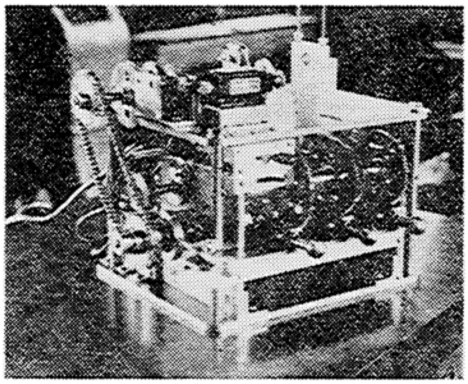

Fig. 1. Automatic titrator

(c) Procedure—0.075 N solution of silver nitrate is added to 50 cc. of 0.001 M/l buffered solution of organic compound in the rate of 0.67 cc./5 min. i.e. 0.00005 M/5 min. under vigorous agitation. In this concentration ratio, five minutes are necessary for an equivalence of Ag. On the other hand, the chart speed of the recorder can be changeable in 5, 10, 20, 60, 120, and 240 mm/min. or mm/hr. Throughout this experiment, the speed 10mm/min. was used, so 50 mm. on the chart corresponds to an equivalent.

If the compound is salted out in buffer solution, it is dissolved in organic solvent as methyl alcohol, then diluted with the buffer solution to the above concentration. A cleaned silver electrode is dipped in the solution and titration is started, and then its potential refered to the saturated calomel electrode is recorded as described above at 50°C.

(d) Buffer Solutions—As buffer solutions, the Walpole's acetate buffers are used for pH 4 and 5, the Sörensen's phosphate buffers for pH 6, 7, and 8, the Sörensen's borate buffers for pH 9, 10, and 11. The formulae for these were given in our previous report[3]. In phosphate buffers, some substances need more silver ions than expected and this showed that the phosphate buffers were inadequate for these substances. So the authors used the citrate buffers for pH 6 and 7, and the modified Sörensen's buffer for pH 8. The formulae of the buffers are given in Table 1.

TABLE I

FORMULAE OF BUFFERS

Sörensen's citrate buffer at 50°C
Solution A
(citric acid 21.008g+I N NaOH 200cc)/1.
Solution B 0.I N NaOH
*p*H 6.0 solution A 52.5 vol% solution B 47.5%
6.8 ,, 61.8 ,, 38.2
Sörensen's glycine buffer at 50°C
Solution A (glycine 7.505g+$NaNO_3$ 8.501g)/1.
Solution B 0.1 N NaOH
*p*H 8.0 solution A 93.5% solution B 6.5%

The sodium chloride of Sörensen's original formula is replaced by a gram equivalent of sodium nitrate to avoid the precipitation of silver chloride. In order to compare the buffering efficiency of the original and modified formulae, the *p*H change at 50°C. is shown in Table 2 when 0.05 N $AgNO_3$ is added to 50 cc. of the buffering solution.

TABLE II

BUFFERING POWER OF TWO BUFFER SOLUTIONS BY ADDITION OF $AgNO_3$

Kind of buffer	0.05N $AgNO_3$cc	0.00	1.00	2.00	3.00	4.00	5.00
glycine	pH	7.97	7.88	7.70	7.50	7.38	7.22
phosphate	pH	7.93	7.90	7.88	7.82	7.80	7.78

The phosphate buffer has a far better buffering power than the glycine buffer.

Results of Experiment

(a) Significance of Silver Potentiometric Titration Curves—As the significance of curves was fully discussed in the previous papers[2,3], the authors intend here to remind the readers of the following.

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[5] S. Kikuchi and Y. Sakaguchi, *Seisan Kenkyū* (in Japanese) published by Univ. of Tokyo, **3** No. 4, 161 (1951).

[6] J. J. Lingane, *Anal. Chem.*, **20** No. 4, 285-292 (1948).

i. The silver potential is likely to be less noble when the silver salt of organic compound is hard-soluble and the compound adheres to silver halide as sensitizer, fog-inhibitor or desensitizer.

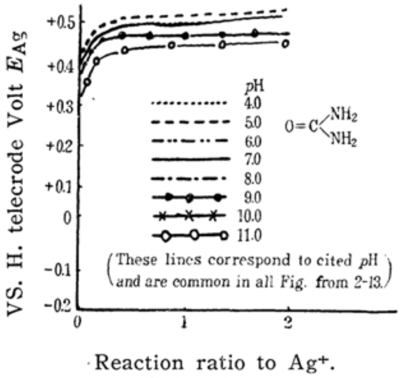
ii. One can discriminate the quality of compounds with their colors of precipitates. Black, brown or grey colors shows the production of silver or silver sulfide which are the reason of sensitization or fogging action. Yellow, yellowish orange, and white colors which are their silver salts are generally the sign for good fog-inhibitors.

iii. The sawteeth form of curve shows the reduction of Ag^+.

iv. The curve of the ineffective substance is same as that of buffer solution.

(b) Potassium Thiocyanate (I) — Potassium thiocyanate gives constant silver thiocyante potentials curves at any pH. The thiocyanate ion is similar to inorganic halogen ions although it contains a sulfur atom.

(c) Urea (XIV), Guanidine (XV) and Diphenyl guanidine (XVI) — From Fig. 2 it may be seen that urea does not react with Ag^+. Guanidine and diphenyl guanidine resemble urea.



Abbreviations

B	black
Br	brown
D	dirty
G	grey
O	orange
P	precipitate
W	white
Y	yellow

Fig. 2. Urea.

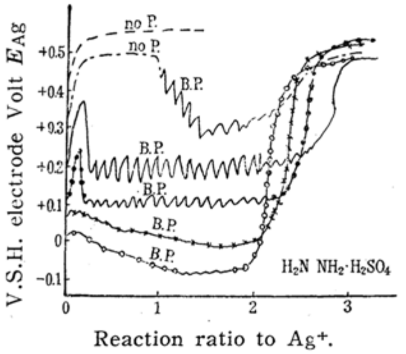


Fig. 3. Hydrazine sulfate.

(d) Hydrazine — The solution of hydrazine sulphate gives, as generally accepted, the curve of reduction of 2 mol. Ag^+ ion in the region more alkaline than pH 6 (Fig. 3).

(e) Thiourea and Thiosemicarbazide—From Fig. 4 the thiourea shows the reduction of 2 mols. of Ag^+ ion in the acid region, while in the neutral and alkaline regions, the curves indicate the decomposition of compound to give black silver sulfide up to 2 mols. equivalent of $AgNO_3$ and the yellow residue with more silver ions. The former is produced by means of $=S$ and the latter by $-NH_2$. The authors suppose that the electronegativity of NH_2 in thiosemicarbazide affects less than thiourea owing to the long distance from the carbon atom attached to $=S$, so the first gives the silver sulfide more easily than thiourea. (Fig. 4, 5)

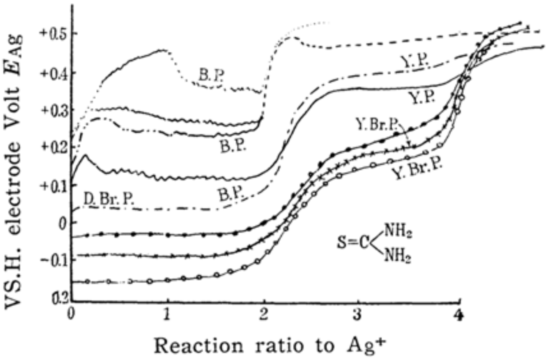


Fig. 4. Thiourea.

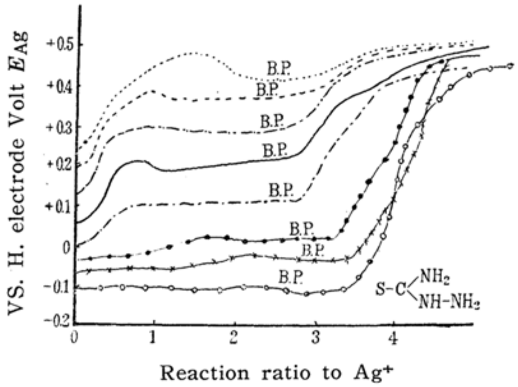
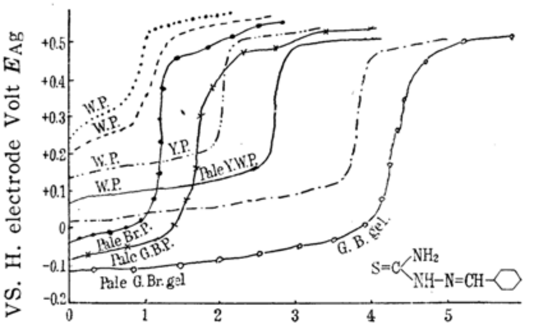
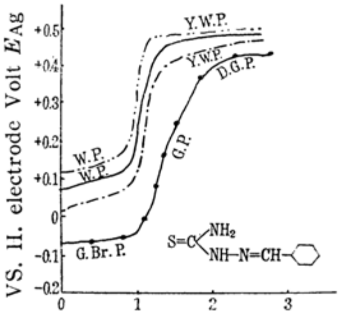


Fig. 5. Thiosemicarbazide.

(f) Benzaldehyde Thiosemicarbazone (IV)—Fig. 6 and 7 are obtained for (IV). In Fig. 6 Sörensen's phosphate buffers were used, the equivalence to Ag^+ becomes larger with pH increase up to 8. The silver equivalent at pH 6, 7, and 8 are 2, 2.5, and 3.5 respectively. Suddenly it turns back to 1 at pH 9. In Fig. 7 where the citrate and the glycine buffers are used, then (IV) gives unit silver equivalent at pH range from 4 to 10, in other word it does not give silver sulfide. In fact, (IV) is the good fog-inhibitor. Perhaps the benzaldehyde group lessons the electronegativity of NH_2 group.



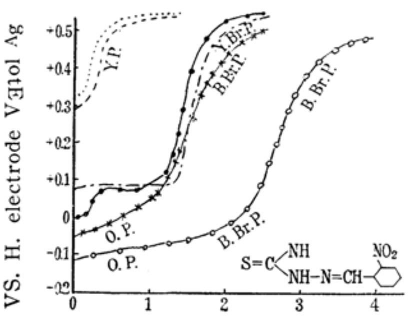
Reaction ratio to Ag^+
Fig. 6. Benzaldehyde thiosemicarbazone.



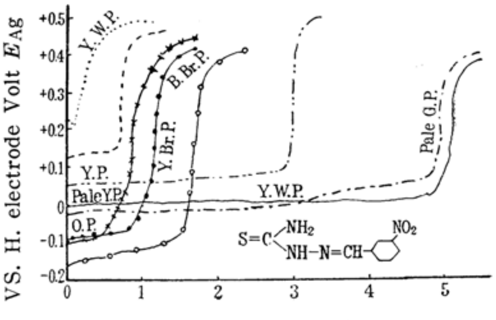
Reaction ratio to Ag^+
Fig. 7. Case of benzaldehyde thiosemicarbazone with new type of buffer solution.

(g) o-, m-, p- Nitrobenzaldehyde Thiosemicarbazones. (VIII, IX, X)—The curves for three isomers (VIII), (IX), (X) are given respectively in Fig. 8, 9, and 10. At pH 6, 7, and 8 (IX) and (X) they need too much silver ion and at pH 9 the equivalence turns back to unity. New buffers reveal that even at these pH the substances need one Ag^+. The substance (VIII) shows, contrary to (IX) and (X), the unit equivalent even with phosphate buffers. This fact makes us to suppose that silver atom, phosphate ion and some organic substance from the complex form and meta and para forms are more suitable for this complex formation than ortho form.

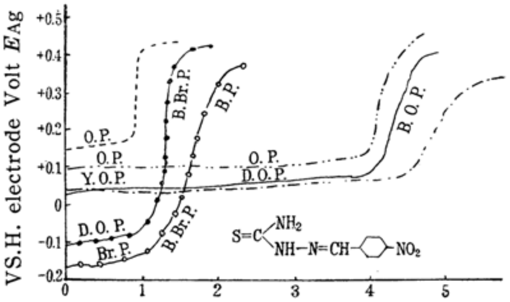
The colors of precipitates show that these compounds are probably good fog-inhibitors. Indeed the emulsion test with these substances done by Konishiroku Photo Co. reveals that these are good fog-inhibitors though a little desensitizing[7].



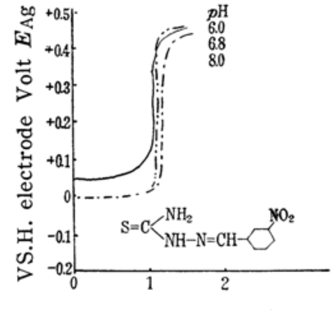
Reaction ratio to Ag^+
Fig. 8. *o*-Nitrobentaldehyde thiosemicarbazone.



Reaction ratio to Ag^+
Fig. 9. *m*-Nitrobenzaldehyde thiosemicarbazone



Reaction ratio to Ag^+
Fig. 10. *p*-Nitrobenzoldehyde thiosemicarbazone.



Reaction ratio to Ag^+
Fig. 11. Case of *m*-nitrobenzaldehyde thiosemicarbazone with new type of buffer solution.

(h) *p*-Dimethylamino Benzaldehyde Thiosemicarbazone (VI) and Phenyl Thiosemicarbazide (XI)—The silver potentiometric titration curves are also obtained for (VI) and (XI). The substance (VI) as predicated from its similar structure with (IV) has no tendency to produce Ag_2S, while substance (XI) has this tendency stronger than thiosemicarbazide (III).

(i) Piperonal Thiosemicarbazone (V) and *p*-Acetamide Benzaldehyde Thiosemicarbazone (VII) and Benzaldehyde Phenyl Thiosemicarbazone (XII)—These compounds have qualities between (IV) and (XI).

(j) The color of the precipitates and the free energy change are shown in Table III when the substances are titrated with Ag^+. To see easily all characters of the tested substances, Table III is dressed in which the symbol $-\Delta F^{\circ}_{323}$ (standard free energy change at 50°C.) is as previous reports[2,3].

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[7] Konishiroku Photo Co., *Report of the Committee of addition agent*, (1952).

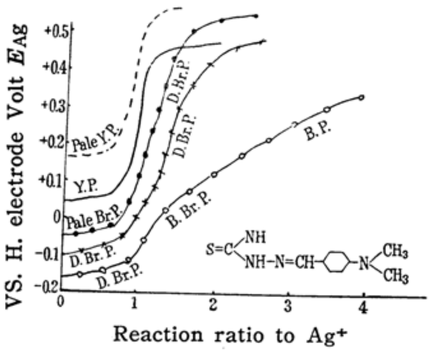

Fig. 12. *p*-Dimethylamino thiosemicarbazone.

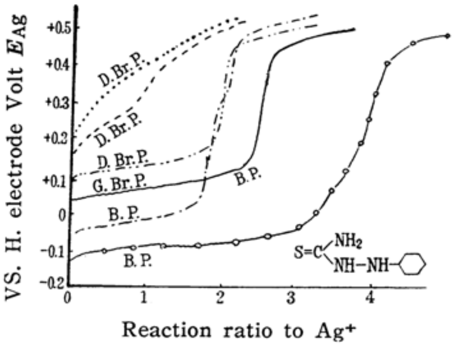

Fig. 13. Phenyl thiosemicarbazide.

TABLE III

PROPERTIES OF SUBSTANCES OBTAINED BY THE REACTION OF ORGANIC SULFUR COMPOUNDS AND THE SILVER ION

Substances	*p*H 5.0		7.0		9.0	
	$-\Delta F^\circ_{323}$ kcal/M	Colors of precipitate	$-\Delta F^\circ_{323}$	Colors	$-\Delta F^\circ_{323}$	Colors
Potassium thiocyanate (I)	15.4	white	15.4	white	15.4	white
urea (XIV)	—	no	—	no	—	no
guanidine (XV)	—	no	—	no	—	no
diphenyl guanidine (XVI)	—	no	—	no	—	no
hydrazine (XIII)	—	no	17–18	silver black ppt.	20	silver black ppt.
thiourea (II)	16	brown, black	19	dirty brown black	22.7	dirty brown, black
thiosemicarbazone (III)	14	brown, black	18	brown, black	22.5	black
benzaldehyde thiosemicarbazone (IV)	17.7	white	20.6	white	22.9	pale greyish brown
piperonal thiosemicarbazone (V)	18.7	white	21.1	white	23.2	pale brown
p-acetamide benzaldehyde thiosemicarbazone (VII)	17.5	white	20	white	22.5	brown black
p-dimethylamino benzaldehyde thiosemicarbazone (VI)	18.9	pale yellow	21.7	yellow	23.5	pale brown
m-nitrobenzaldehyde thiosemicarbazone (VIII)	18.3	yellow	20.8	yellow	23.0	pale brown
phenyl thiosemicarbazide (XI)	18.8	dark brown	20.7	greyish brown	23.5	black
benzaldehyde phenyl thiosemicarbazone (XII)	19	pale yellow	21.5	yellow	22.9	yellow brown

Conclusion

From the silver potentiometric titration of some organic sulfur compounds and their related compounds, the following facts are revealed.

1. In the phosphate buffer, some compounds (IV, V, VIII, X, XII) need too much silver ion because of the complex from of silver and phosphate and these compounds. Then the citrate and glycine buffers were used in order to avoid the complex formation from these compounds.

2. SCN^- radical gives an inorganic silver salt which is not affected with the *p*H change.

3. Hydrazine reduces Ag^+ although it does not give sulfur compound, because of the reducibility of NH_2.

4. Phenyl thiosemicarbazide (XI) gives sulfur most easily, next is thiosemicarbazide (III) and then thiourea (II).

5. We concluded that the sulphur atom is necessary to make good fog-inhibitors, and thiosemicarbazone derivatives which have long chain structure are excellent for the decrease of the electronegativity of NH_2. Thiosemicarbazide derivatives give sulfur compounds and thiocyanate gives silver thiocyanate only.

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