On the Properties of 1-Thiol-benzthiazole Derivatives as Photographic Addition Agents

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Introduction

Previously the author reported several times about the derivatives of 2-mercapto-benzimidazole as addition agents for photographic emulsions and developers.[1],[2],[3],[4]

In this connection he has been examining from that time the probabilities or the properties as additions of 1-thiol-benzthiazole, usually called 2-mercapto-benzthiazole, intimately related compound of the above mentioned, and soon the practical importance of this compound in photography has been recognized.

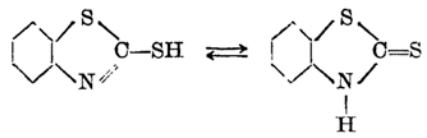
It is interesting to know that the usefulness of this compound has been recently disclosed in other countries.[5],[6]

The author's intention, being interrupted with the short supply of materials during the war, to prepare and examine those derivatives of it, as were derived of 2-mercapto-benzimidazole, is now attained.

In this report, properties of two kinds of alkyl (and aralkyl) derivatives of this compound are described as additions in developer for pure silver chloride emulsion and as additions in emulsion for chloride and chloro-bromide emulsions and compared with similar derivatives of mercapto-benzimidazole already reported.

Relation between S-Alkyl- and N-Alkyl-derivatives

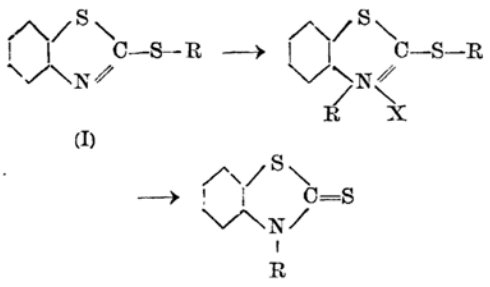
1-Thiol-benzthiazole is a single substance having two tautomeric configurations by proton transfer as shown below,



but those compounds, in which this replaceable hydrogen atom is substituted by alkyl (or aralkyl) radical, form two distinct compounds, S-alkyl-derivatives (I) and N-alkyl-derivatives (II), each must be called 1-alkylthio-benzthiazole (I) and 1-thio-2-alkyl-1:2-dihydro-benzthiazole (II), and it is not easy to convert one to the other.

Generally (II) is more stable than its corresponding compound of (I), and (I) can be converted to (II) through its quaternary ammonium salt

(1) Yasushi Oh-yama, *Bull. Inst. Phys. Chem. Research (in Japanese)*, **22**, 483 (1943).
(2) Yasushi Oh-yama, *ibid.*, **23**, Chem.-7 (1944).
(3) Yasushi Oh-yama, *J. Soc. Scientific Photography Japan (in Japanese)*, **9**, 1 (1943).
(4) Yasushi Oh-yama, *ibid.*, **9**, 57 (1943).
(5) A. Bycichin and L. Vlach, *Chem. Listy*, **41**, 136; *Sci. Ind. Phot.*, **18**, 33; *C. A.* **42**, 1518 (1948).
(6) W. H. Dimsdale and R. R. Robinson (Ilford Ltd.), U. S. P. 2, 432, 864; U. S. P. 2, 432, 865.



(I)

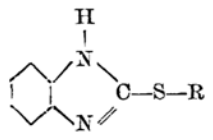
(II)

or by other means. And it is also possible to change its alkyl radical on this occasion.[7]~[10]

Experimental

In homologues of S-alkylthio-benzthiazole (I), methyl, ethyl, allyl, benzyl and carboxymethyl-derivatives, and in those of N-alkyl-compounds (II), methyl, ethyl, allyl[11] and benzyl derivatives were prepared and tested.

The similar S-alkyl-derivatives (III) of mercapto-benzimidazole



(III)

(*i. e.*, 2-thiol-benzimidazole), which were previously reported[1],[3], were tested in comparison with these compounds.

Strips of specially made gaslight paper which was coated with pure silver chloride-gelatin emulsion, were exposed at a fixed condition under optical wedge, developed 1 min. at 20°C., in an ordinary developer containing metol, hydroquinone, sodium sulphite, sodium carbonate but not potassium bromide and finally added varied amounts of above mentioned compounds dissolved in methanol (0.1~1%).

The relation between the time of appearance of images, the fog, the tone of images and the amount of substances added were examined.

The emulsion tests of these compounds were also carried out in some case of gaslight and chloro-bromide emulsions.

Results

Results of above experiments were illustrated in Fig. 1, Fig. 2 and Table 1:

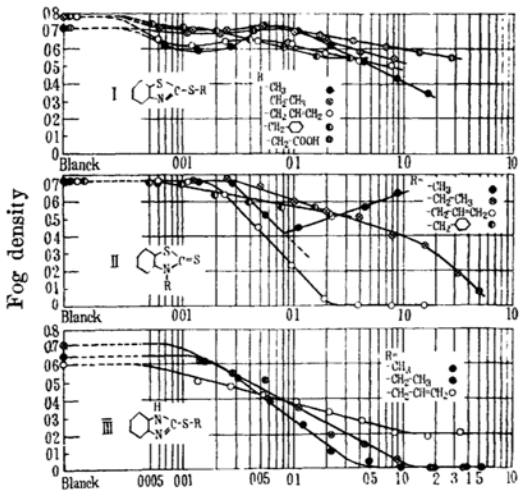


Fig. 1.—Relation between fog-density and concentration of addition in developer.

Table 1

Blue-black Developing Property of Derivatives of 1-Thiol-benzthiazole and 2-Thiol-benzimidazole

Substance added in developer	Minimum conc. to produce appreciable effect	Concentration to produce maximum effect	Bluishness of tone
1-Methylthio-denzthiazole	0.027< C <0.055	0.44 (approx.)	+
1-Ethylthio- 〃	0.025< C <0.051	0.20~0.40	+
1-Allylthio- 〃	0.024 (approx.)	0.39 (approx.)	++
1-Benzylthio- 〃	0.32 (approx.)	?	very weak
1-Thio-2-methyl-1:2-dehydro-benzthiazole	0.027< C <0.055	0.44 (approx.)	++++
1-Thio-2-ethyl-1:2- 〃	1.60< C <3.20	?	++
1-Thio-2-allyl-1:2- 〃	0.006< C <0.012	0.77 (approx.)	+++
1-Thio-2-benzyl-1:2- 〃	0.08 (approx.)	0.16 (〃)	very weak
2-Methylthio-benzimidazole	0.015< C <0.030	0.48 (approx.)	+
2-Ethylthio- 〃	C <0.014	0.45 (〃)	+
2-Allylthio- 〃	C <0.013	0.42 (〃)	+++

(7) C. Hasan and R. F. Hunter, *J. Chem. Soc.*, **1936**, 1672.
(8) J. D. Kendall (Ilford Ltd.), F. P. 821, 980; B. P. 475, 647.
(9) W. A. Sexton, *J. Chem. Soc.*, **1939**, 470.
(10) F. P. Reed, A. Robertson and W. A. Sexton, *J. Chem. Soc.*; **1939**, 473.
(11) Melting point of this compound (1-thio-2-allyl-1:2-dihydro-benzthiazole) is 66.5~67.0°C.

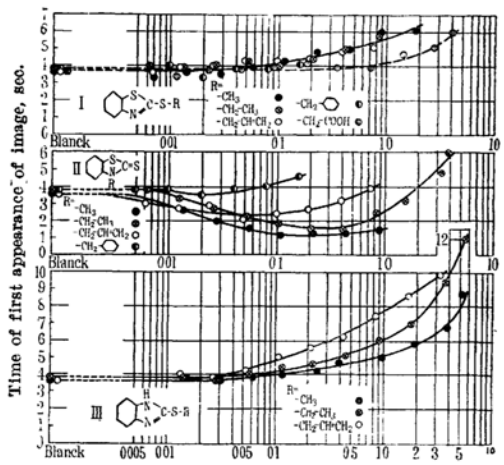


Fig. 2.—Relation between time of first appearance of image and concentration of addition.

Behaviors of these additions when added in emulsion, though these tests were not carried out systematically, keep parallel with those tendency they presented when added in developer. And it would be able to conclude as follows.

(A) Anti-fogging or Fogging Properties.—All of these compounds have fog-preventing or fog reducing property. Generally most of N-alkyl compounds (II) of 1-thiol-benzthiazole surpass even the marked fog-preventing property of any of the S-alkyl derivatives of 2-thiol-benzimidazole (III), on the contrary the S-alkylthio-benzthiazole (I) are inferior compared with the above mentioned and almost equal with its parent substance (1-thiol-benzthiazole).

The only exception is the methyl derivative of (II), which exhibits fog-preventing property at low concentration in developer and causes a considerable degree of fog at high concentration, and this tendency can also be seen when added in emulsion. The emulsion which contains such an amount of it that restrains fog when prepared, sometimes becomes heavily fogged during the storage or incubation test.

The ethyl or allyl derivative of (II) is not only good as a fog-reducer in developer, but can give the emulsions of very good durability. Similarly the benzyl derivative which cannot exhibit a noticeable effect in developer owing to its low solubility, can restrain fog and increase durability when added in emulsion.

(B) Blue-black-developing Property.—The tone or color of the developed silver image of chloride or chloro-bromide emulsion turns from neutral black or warm-black to blue-black, when most of these derivatives (I, II and III) are added in developer or in emulsion, and this property cannot be seen in their parent substances.

This tendency differs according to the substituents, in (I) and (III) it grows stronger when the alkyl radical is replaced by methyl, ethyl, allyl in turns, but benzyl derivatives of these are very weak probably because of their low solubility, and carboxymethyl ($-CH_2-COOH$) derivatives show no effect.

On the contrary N-methyl, ethyl and allyl derivatives (II) of this dihydro-benzthiazole show equally very strong blue-black developing effect, even the benzyl derivative of it, being very weak in developer, shows fairly good effect when added in emulsion.

(C) Development Accelerating or Retarding Property and Sensitizing or Desensitizing Effect.—Derivatives of (I) and (III) series retard development more or less, and derivatives of (II) series, to the contrary, accelerate it.

Plotting the time of first appearance of image against the concentration in developer of these additions (Fig. 2), it shows characteristic curves for each series (I, II and III) and in series (II) and (III) their effects differ regularly according to the number of carbon atoms in the substituted alkyl radical *e. g.*, methyl, ethyl, allyl, benzyl in turns, while in series (I) they bear no evidence of this difference except the carboxymethyl derivative.

The sensitizing and desensitizing properties of them in emulsions run parallel with their development accelerating and retarding properties, (II) has somewhat sensitizing property for silver chloride emulsion as one of the thions which Kendall[12] already pointed out, and derivatives of series (I) and (III) show rather desensitizing effect but not noticeable in ordinary case.

Discussion

The similarity of actions of (I) and (III) lies in parallel with the resemblance of their constitution, and it is supposed to be attributable to the imino group in the imidazole ring of (III) that it exceeds (I) in fog-preventing property and development retardation.

It is recognized from blue-black developing property of these three series, that the imino radical gives scarcely any effect upon this property and the relation between this property and development retardation is not basic.

The considerable difference between (I) and (II),

(12) J. D. Kendall, IXth. Cong. Phot. 1935, Paris, 235.

which is the influence of the same substituent in different positions of the molecule, is supposed mainly to be attributable to the change of the constitution of the sulfur atom of thio-ether type to more reactive thio-keto type.

It is easy to point out this thio-keto radical as the cause of sensitizing, development-accelerating or fog-preventing property of (II).

The sulfur atom of this radical forms complex with silver or silver salts and the stability, the solubility, the rate of decomposition or the delicate combination of those character of this complex compound will be the cause of complicated, sometimes contradictory behavior of these compounds as additions. The behavior of methyl derivative of the series (II) surely indicate the lack of this stability of the complex compound between the said derivative and silver chloride.

Summary

S-Alkyl-(I) and N-alkyl-derivatives (II) of 1-thiol-benzthiazole are prepared and tested as additions for silver chloride emulsions, and compared with previously reported S-alkyl-derivatives (III) of 2-thiol-benzimidazole. Properties of these substances as additions may differ according to alkyl radicals substituted, positions of substitution and their parent substances.

(1) Most of these compounds (I, II and III) show blue-black developing property which can not be seen in parent substances. This effect is the weakest in (I) and the strongest in (II), and as a whole, being the substituent methyl, ethyl or allyl, its activity rises in turn. Benzyl derivatives of them are almost inactive and carboxymethyl derivatives of (I) and (III) are inactive.

(2) As for the fog-preventing property, (II) and (III) have greater activity and increase activity as the number of carbon atoms in the substituent increases. (I) is not so active as (II) or (III) regardless of its substituents.

(3) It is remrakable that (II) has somewhat sensitizing property added in emulsion, and accelerate the development when both (I) and (III) retard it.

(4) The similarity of actions of (I) and (III) lies in parallel with the resemblance of their chemical constitution, but (I) is inferior to (III) in those properties which are supposed to be due to the imino group in the imidazole ring, as fog-preventing action.

(5) The considerable difference between (I) and (II) which is the influence of the same substituent in different position of the molecule, is supposed to be attributable to the change of the constitution of the sulfur atom of thio-ether type to more reactive thio-keto type. The sensitizing, fog-preventing or development-accelerating action of the latter is supposed to be intimately related to the complex forming character of this thio-keto group with silver or silver salts.

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