[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WASHINGTON]

Additive Compounds Formed in the Desulfurization of Thioureas by Copper Hydroxide

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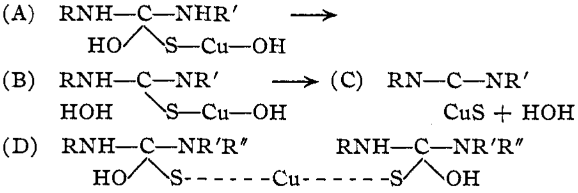
Though numerous reagents have been used to desulfurize thioureas, no intermediate additive compounds have been observed or reported. Usually the color of the metallic sulfide masks the color of the intermediate compound. In the foregoing contribution, in which desulfurization of the thiourea was effected by lead hydroxide, orange, red and brown products were observed before the blackness of lead sulfide was developed. It was suspected that these colors indicated intermediate additive compounds but, owing to formation of mixtures with lead hydroxide, no separation could be made. Most of the other metal hydroxides gave only the colors of the respective metal sulfides.

With concentrated Fehling solution, however, certain thioureas gave microcrystalline, brilliantly colored compounds that could be isolated before copper sulfide was formed. They proved to be additive compounds of one or two molecules of the thiourea with one molecule of copper hydroxide. Thioureas of the type RNH·CS·NHR′ unite as RNH·CS·NHR′·Cu(OH)$_2$. Thioureas of the type RNH·CS·NR′R″ unite as (RNH·CS·NR′R″)$_2$·Cu(OH)$_2$. The former can be depicted structurally as (A); the latter, as (D).



Proofs of (A), (B) and (C) were obtained when the thiocarbaniline compound was heated mildly. The red color changed to yellow and one molecule

TABLE I

No.	Compn. of thiourea	Colors	Decompn. t's	Copper, % Calcd.	Copper, % Found
		TU·Cu(OH)$_2$			
1	Thiourea	Gr. ocher	90–100	36.59	35.31
2	Phenylthiourea	Yellow	105	25.49	
3	Thiocarbanilide	Orange	98–100	19.50	10.76
4	*s*-Di-*o*-tolylthiourea	Orange	105–120	17.93	18.10
5	*s*-Di-*m*-tolylthiourea	Yellow	115–140	17.93	18.28
6	*s*-Di-*p*-tolylthiourea	Brown	100–120	17.93	17.94
7	*m*-Tolyl—NH—CS—NH—*o*-tolyl	Orange	105–120	17.93	18.59
8	*m*-Tolyl—NH—CS—NH—*p*-tolyl	Orange	105–120	17.93	17.89
9	PhNH—CS—NH—*p*-tolyl	Orange	95–100	18.71	18.50
10	PhNH—CS—NH—CH$_3$	Brown	100–125	24.10	24.18
11	PhNH—CS—NH—C$_2$H$_5$	Purple	125–135	22.88	23.10
12	PhNH—CS—NH—C$_4$H$_9$—*n*	Red-yl.	95–100	20.78	21.17
13	PhNH—CS—NH—C$_6$H$_4$—N(CH$_3$)$_2$	Ocher	120–135	17.35	17.07
14	PhNH—CS—N(CH$_3$)Ph	Red	125–215	18.71	18.88
15	PhNH—CS—NH—cyclohexyl	Purp. red	120–130	11.23	11.36
		TU·Cu(OH)$_2$–H$_2$O			
16	PhNH—CS—NH—C$_6$H$_4$OC$_2$H$_5$—*o*	Red	125–145	18.06	18.10
17	Thiocarbanilide	Orange	98–100	20.65	20.56
18	Allyl-NH—CS—NH—Ph	Orange	95–103	23.38	23.48
19	Allyl-NH—CS—NH—*o*-tolyl	White	116–125	22.23	22.06
20	Allyl-NH—CS—NH—*m*-tolyl	Ocher	110–125	22.23	22.01
21	Allyl-NH—CS—NH—*p*-tolyl	Yellow	120–125	22.23	22.05
		(TU)$_2$·Cu(OH)$_2$			
22	Allyl-NH—CS—N(C$_4$H$_9$)$_2$—*n*	Brown	133–145	11.46	11.39
23	PhNH—CS—N(CH$_3$)Ph	Chocolate	150	10.90	10.71
24	PhNH—CS—N(C$_2$H$_5$)Ph	Br. black	150	10.40	10.95
25	PhNH—CS—piperidine	Chocolate	140–170	11.21	11.11
26	*o*-Tolyl—NH—CS—N(CH$_3$)Ph	Chocolate	155	10.42	10.73

TABLE II

Name	Formula	Crystals	Melting point, °C.	Sulfur, % Calcd.	Sulfur, % Found
Allyl-*m*-tolylthiourea	$C_{11}H_{14}N_2S$	Prisms	66	15.54	15.39
Allyl-di-*n*-butylthiourea	$C_{12}H_{24}N_2S$	Prisms	83	14.39	14.33
Phenylcyclohexylthiourea	$C_{13}H_{18}N_2S$	Plates	150	13.67	13.80
Phenyl-*n*-butylthiourea	$C_{11}H_{16}N_2S$	Prisms	85	15.31	15.48
m-Tolyl-*p*-tolylthiourea	$C_{15}H_{16}N_2S$	Needles	148	12.50	12.44
m-Tolyl-*o*-tolylthiourea	$C_{15}H_{16}N_2S$	Leaflets	151	12.50	12.70

of water was eliminated. At 100° it melted, blackened, gave off water and yielded diphenylcarbodiimide. The additive compound (A) in benzene with aniline, or with other primary bases, yielded by heating on the water-bath triphenylguanidine or other guanidines, thus proving the intermediate formation of diphenylcarbodiimide as in (C).

Compounds of the type (D) do not decompose easily to yield copper sulfide; hence they are readily prepared. The compound $(PhNH-CS-NMePh)_2 \cdot Cu(OH)_2$ yielded by heating at 150° or by heating in benzene with aniline, beautiful dichromate-like colored crystals that proved to be $PhNH-CS-NMePh \cdot Cu(OH)_2$. It and other compounds of this type will be investigated.

Experimental Part

The Fehling solutions used in the preparation of these copper hydroxide compounds possessed the usual composition for the Rochelle salt solution but the copper sulfate solution was five times as concentrated. Approximately equal volumes of these gave clear solutions. A saturated solution of the thiourea in acetone was added to a bottle containing the mixed Fehling solutions. The contents of the bottle was agitated by hand or by a mechanical shaker until a voluminous precipitate was formed. This precipitate is usually suspended in the acetone and this mixture can be decanted and filtered. Or the copper compound can be filtered on a Büchner funnel and the filtrate returned to the bottle for formation of another crop. The solid on the funnel is washed first with water to remove copper sulfate solution and then with acetone to remove precipitated thiourea. After drying, the additive compounds can be analyzed easily by ignition to copper oxide.

All of these compounds decompose and blacken at various elevated temperatures, yielding insoluble copper sulfide and liquid carbodiimides, hence they do not possess true melting points. These decomposition points are only approximately characteristic. Compounds of type (D) require higher temperatures for decomposition and are transformed to compounds of type (A) at temperatures lower than that of decomposition to form copper sulfide. The compounds most commonly form aggregates of prisms. Initially some form oily drops that solidify on standing, hence the crystals are often ill defined. On heating or exposing to air most of these compounds change color, indicating loss of one molecule·of water. The allyl compounds spontaneously lose this water as they are prepared.

The new thioureas in Table II were prepared from the mustard oil indicated by the first group and the base as indicated by the second group.

Summary

The mechanism of oxidation of thioureas by copper hydroxide has been determined. The addition compounds first formed lose water and subsequently decompose to yield another molecule of water, copper sulfide and carbodiimides. Analogous reactions probably are involved in the desulfurization of thioureas by other metal hydroxides.

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