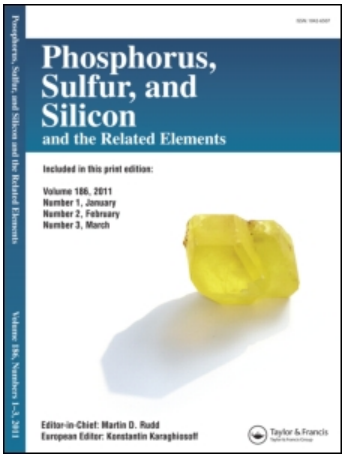

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IDENTIFICATION OF YELLOW COLOR FORMED FROM REACTION OF CARBON DISULFIDE AND ALUMINA

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IDENTIFICATION OF YELLOW COLOR FORMED FROM REACTION OF CARBON DISULFIDE AND ALUMINA

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ABSTRACT

The water-soluble yellow substance formed by the reaction of alumina and carbon disulfide first reported by Perry in 1925 is identified as sodium trithiocarbonate and/or sodium hydrogen trithiocarbonate (depending on the pH) on the basis of comparative electronic absorption spectra and chemical tests. Electronic absorption spectra of sodium tri- and tetrathiocarbonates under various conditions are reported.

Introduction

Perry[1] was apparently the first to report the formation of a yellow color during the absorption of carbon disulfide vapor by alumina gel. Munro and McCubbin[2] later found that the yellow color dissolved in water and concluded on the basis of chemical tests that it was due to sodium disulfide which was formed by the reaction of carbon disulfide with sodium hydroxide absorbed on the alumina. On the basis of marked differences in uv absorption spectra it was later shown[3] that the yellow substance was not sodium disulfide, the spectrum of the yellow substance having maxima at 398 and 325 nm and the sodium disulfide spectrum having shoulders at 360-375 and 290-300 nm. We now wish to report later work which identifies the yellow substance as mainly sodium trithiocarbonate, Na_2CS_3, and/or sodium hydrogen trithiocarbonate, $NaHCS_3$ (depending on the pH).

Results and Discussion

The possibility was first considered that the yellow color might result from sodium trithiocarbonate formed from the reaction of sodium sulfide with carbon disulfide (eq. 1). Munro and McCubbin[2] suggested previously that hydrogen sulfide could be

$$Na_2S + CS_2 \rightarrow Na_2CS_3 \qquad (1)$$

formed by hydrolysis of carbon disulfide. Hydrogen sulfide would then be converted into sulfide by reaction with hydroxide. Sodium sulfide has been detected[4] as a transient intermediate during the viscose aging process which involves a side reaction of carbon disulfide and sodium hydroxide. Since sodium tetrathiocarbonate is also known and could be formed analogously by the reaction[5] of sodium disulfide and carbon disulfide (eq 2) this possibility was also investigated.

$$Na_2S_2 + CS_2 \rightarrow Na_2CS_4 \qquad (2)$$

Uv spectra of aqueous solutions of sodium trithiocarbonate and sodium tetrathiocarbonate were compared with those of the yellow product from the reaction of alumina and carbon disulfide. Several problems were encountered in attempting to make an exact comparison: (1) The concentration of the yellow substance was unknown so molar absorptivities (ϵ) could not be compared. (2) Samples of the yellow substance contained carbon disulfide which could not be entirely removed without destroying[6] the yellow color. (3) The spectra of the aqueous solutions showed a time dependence. (4) The possibility of complication from atmospheric oxidation was considered. (5) A concentration effect on the spectra was noted.

The factors mentioned were all investigated to determine the importance of each and as to how any variables might be controlled. Although the concentration of the yellow substance was unknown, concentrations were made comparable by dilution with solvent judging from absorbance measurements. To compensate for the presence of some carbon disulfide in samples of the yellow substance, dilutions of the yellow substance, and sodium tri- and tetrathiocarbonates were made with carbon disulfide-saturated water as well as distilled water alone to examine the effect if any of this factor[7] on the spectra. The presence of carbon disulfide would repress any possible dissociation of the thiocarbonates according to equilibrium (3). Since the spectra showed changes on standing, comparisons were

$$Na_2CS_{x+2} \rightleftarrows Na_2S_x + CS_2 \qquad (3)$$

made with freshly prepared solutions to minimize this factor. Since hydrolysis of thiocarbonate ion might be expected (eq 4), spectra of basic solutions were also

$$CS_{x+2}^{2-} + H_2O \rightleftarrows HCS_{x+2}^{-} + OH^- \quad (4)$$

studied since hydrolysis has been reported[9,10] to be retarded in the presence of sodium hydroxide. The effects of possible atmospheric oxidation were investigated by comparisons of samples prepared in inert nitrogen atmospheres with those prepared under ordinary conditions and the effect of passing oxygen through the solutions for varying periods of time. In summary, knowledge of the variables made it possible to keep these under control so that comparisons of spectra of samples under comparable conditions could be made.

Electronic absorption spectra for trithiocarbonate solutions have been previously reported. These are collected in Table I for comparison and assessment. Müller and coworkers[11] identified the maxima at 500, 336, and 223 nm having ϵ values of 30, 1.0×10^4, and 1.0×10^4 respectively for the trithiocarbonate ion in water as the following transitions respectively: $n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$ and $n \rightarrow \sigma^*$ (tentatively). Seidel[12] reported maxima at 500 nm (20,000 cm^{-1}) and 395 nm (25,300 cm^{-1}) for reflectance spectra on solid sodium trithiocarbonate and assigned these as $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions respectively. For sodium tetrathiocarbonate, two peaks were reported[10] at 400 and 320 nm.

From the table it is clear that the main difference between the tri- and tetrathiocarbonates is the presence of the low intensity long wave absorption at 500 nm for the former. In the present investigation, both sodium tri- and tetrathiocarbonates were prepared and the electronic spectra measured, taking into account the factors described above. The data for freshly prepared solutions are collected in Table II. The observed absorption bands for sodium trithiocarbonate are generally in accord with the spectra reported by Atsuki and Takata[13] and Ingram and Toms.[10] The peak at 402 nm in the spectra of the aqueous solutions of sodium trithiocarbonate was markedly decreased to a shoulder. This observation appears to indicate that this absorption may be due to a hydrolysis product which is repressed in the freshly prepared basic solutions. This would be in accord with the reports of Dyer,[14] Müller, *et al.*[11] and von Halban.[15] The lowest wavelength band at 223 reported by Dyer and at 226 by Müller, *et al.* for sodium trithiocarbonate was not observable in the present investigation with the instrument used. The two bands for sodium tetrathiocarbonate at 400 and 320 nm reported by Ingram and Toms[10] checked very closely in the present investigation under various conditions (401–402 and 320–321 nm).

Because of the absorption of the yellow product from the alumina–carbon disulfide reaction at 500–510 nm (which was not observed previously[3] because of its low ϵ value) it seemed evident that sodium trithiocarbonate was a major component of the solution. Since the absorption spectrum of the yellow substance did not quite match any of the spectra of the sodium trithiocarbonate solutions exactly, it was considered that one or more other compounds might be present in addition to the trithiocarbonate. From a comparison of the spectra (Table II) the additional presence of sodium tetrathiocarbonate was thought to be possible. The presence of the latter would modify the appearance of the absorption bands in the 400 and 320 nm regions.

TABLE I

Electronic Absorption Spectra of Thiocarbonates

Compound	Solvent	λ (nm)[a]				Refs.
Na_2CS_3	H_2O	500	400–417	323–325		13
Na_2CS_3	H_2O	500	375–400 (sh)[b]	325–330		10
Na_2CS_3	–	500 (40)	400	332 (1.82×10^4)[c]	226 (8.6×10^3)	14
Na_2CS_3	H_2O	500 (30)	–	336 (1.0×10^4)	223 (1.0×10^4)	11
Na_2CS_3	solid[d]	500	395			12
$BaCS_3$	H_2O (basic)	495 (*ca.* 40)	–	325 (1×10^4)		15
$BaCS_3$	solid[d]	455	388			12
Na_2CS_4	H_2O	–	400	320		10

[a] Wavelength; ϵ in parentheses.

[b] sh = shoulder.

[c] Also shoulder at 320 nm.

[d] Reflectance spectrum.

TABLE II

Electronic Absorption Spectra of Sodium Tri- and Tetrathiocarbonate and Yellow Product from Reaction of Alumina and Carbon Disulfide

Compound	Solvent	$M^a \times 10^3$	Time[b]		λ (nm)[c]	
Na_2CS_3	H_2O	8.30	3 min	503 (30.4)	[d]	[d]
Na_2CS_3	H_2O	0.200	3 min	[e]	402	327–330
					(1×10^3)	(1.00×10^4)
Na_2CS_3	CS_2–H_2O	8.30	3 min	503 (30.4)	[d]	[d]
Na_2CS_3	CS_2–H_2O	0.200	5 min	[e]	402	323–325
					(4.15×10^3)	(1.45×10^4)
Na_2CS_3	1 N NaOH	10.00	3 min	502 (30.4)	[d]	[d]
Na_2CS_3	1 N NaOH	0.100	3 min	[e]	394–398 sh	319
					(1.45×10^3)	(3.02×10^3)
Na_2CS_4	H_2O	0.600	6 min	–	402	320
					(4.90×10^3)	(4.90×10^3)
Na_2CS_4	CS_2–H_2O	0.300	3 min	–	401	321
					(4.26×10^3)	(6.31×10^3)
Na_2CS_4	1 N NaOH	0.100	3 min	–	401	321
					(4.47×10^3)	(2.69×10^3)
Yellow product	H_2O	–	3 min	500–510[f]	400	321
Yellow product	CS_2–H_2O	–	3 min	500–510[f]	401	321

[a] M = molarity.

[b] Time after adding solvent.

[c] Wavelength; ϵ in parentheses.

[d] Total absorption for this concentration at these wavelengths.

[e] Not observed at this concentration.

[f] Band observed at higher concentration; not well-resolved.

Chemical Tests

Hirschkind[16] in 1925 reported a chemical test to detect the presence of trithiocarbonate in a xanthate solution. According to the test, when some 10% lead acetate is added to a 2% xanthate solution, if the precipitate which forms immediately has a red or brown color, thiocarbonate is indicated. In the present investigation tests were carried out with authentic trithiocarbonate as well as tetrathiocarbonate for comparison with the yellow substance from the alumina-carbon disulfide reaction. Although the nature of the phenomenon is unknown, the tests provided useful information. The results with both dilute and concentrated solutions are in Table III. It is evident from the results that the presence of tetrathiocarbonate in moderate amounts is not indicated. Since the colors of the precipitates from trithiocarbonate and the yellow substance did not match exactly, other possibilities were considered. It seemed reasonable that the color might be dependent on the pH of the solution and so tests were carried out in which varying amounts of dilute hydrochloric acid were added to measured amounts of thiocarbonate solutions just preceding the lead acetate addition. These results are also in Table III. From these results also, tetrathiocarbonate is excluded as a major component. Qualitatively, the results favor trithiocarbonate and indicate the presence of hydrogen trithiocarbonate ion, HCS_3^- in equilibrium with trithiocarbonate, the relative concentrations depending on pH. This ion has been referred to by previous workers.[10] As has been pointed out[10] when mineral acid is added to trithiocarbonate, the products vary according to the concentrations, temperature and the acidity. In view of this, exact correspondence of results would be difficult to achieve.

In confirmation of the chemical tests, spectra were obtained on solutions of tri- and tetrathiocarbonates to which varying amounts of dilute hydrocloric acid were added. Qualitatively the results confirm the conclusions from the chemical tests. The most notable feature of the spectra was a change in the 500 nm band

TABLE III

Hirschkind Test: Reaction of Lead Acetate with Tri- and Tetrathiocarbonates and Yellow Substance from Alumina-Carbon Disulfide Reaction

Solution	Result
Na_2CS_3 (conc) (orange)	dark-brown ppt
Na_2CS_3 (dil) (yellow)	red-brown ppt
Na_2CS_3 (very dil)(Pale yellow)	orange-red ppt
Na_2CS_4 (conc)(Yellow)	black ppt & "metallic" mirror
Na_2CS_4 (dil)(Yellow)	black ppt & "metallic" mirror
Na_2CS_4 (very dil)(Pale yellow)	very dark-red black ppt
Yellow substance (conc)	light orange ppt
Yellow substance (dil)	orange-yellow ppt
Na_2CS_3 (dil) + 1 drop 0.05 N HCl	Orange ppt
Na_2CS_3 (dil) + 2 drops 0.05 N HCl	Light orange ppt
Na_2CS_3 (dil) + 3 drops 0.05 N HCl	Orange-yellow ppt
Na_2CS_3 (dil) + 5 drops 0.05 N HCl	Yellow ppt
Na_2CS_4 (dil) + 1 drop 0.05 N HCl	black ppt & silver mirror
Na_2CS_4 (dil) + 2 drops 0.05 N HCl	brownish-black ppt
Na_2CS_4 (dil) + 3 drops 0.05 N HCl	reddish-brown ppt

of the trithiocarbonate with added acid until it resembled closely the band observed for the yellow substance from the alumina-carbon disulfide reaction.

Ingram and Toms[10] suggested the presence[17] of partial hydrolysis products such as COS_3^{2-} to account for changes in their spectra and isolated crystalline needles from the reaction of carbon disulfide and sodium hydroxide to which the formula, $Na_2H_2COS_2$ was assigned. Other workers[18] suggested the occurrence of COS_2^{2-}. It is possible that small amounts of one or more partial hydrolysis products such as these could modify the spectra in the present case. Since such products have not yet been definitely characterized, no definitive statements on this can be made at present. In summary, the evidence indicates that the yellow product from the reaction of carbon disulfide and alumina consists mainly of sodium trithiocarbonate and sodium hydrogen trithiocarbonate with the possible presence of small amounts of other partial hydrolysis or oxidation products.

Experimental Section

The Yellow Reaction Product

Solutions of the yellow reaction product from alumina and carbon disulfide were prepared in the following way. Alumina was shaken with purified carbon disulfide for varying periods of time. The carbon disulfide was decanted and water (or carbon disulfide-saturated water) was added. The mixture was shaken and filtered.

Alumina

Most of the work was done with Merck chromatographic absorption grade (80–200 mesh). In some experiments, Fisher chromatographic grade and Fisher activated grade (8–14 mesh) were also used.

Carbon Disulfide

ACS grade carbon disulfide was purified by the method of Riddick and Toops.[19] The same results were obtained when the material was purified by a simple distillation just before use.

Sodium Trithiocarbonate

Sodium trithiocarbonate was prepared by the following three procedures.

(1) *Sodium sulfide-carbon disulfide method.* Sodium sulfide nonahydrate ($Na_2S \cdot 9H_2O$) (0.144 g, 6.00×10^{-4} mol) was stirred in a stoppered container by means of a magnetic stirring bar[20] with an equimolar weight of carbon disulfide (0.0457 g) for 6 hrs. This length of time was found to be adequate for complete reaction as evidenced by maximum absorption in the spectra. A solvent (distilled water, carbon disulfide-saturated water, or a basic solution) was then added with shaking and the resultant solution was poured into a volumetric flask, adding the washings and diluting to the desired volume. This solution was used for spectrophotometric studies. Time was measured from the addition of solvent. In many of the experiments the reactions were carried out in a nitrogen atmosphere to investigate the effect of possible oxidation.

(2) *Sodium hydroxide-carbon disulfide method.* Carbon disulfide was stirred with excess concentrated sodium hydroxide solution for 6 hours as described above and then diluted with water or aqueous base to the desired concentration (based on sulfur content, assuming complete conversion to trithiocarbonate).

In some experiments when sodium hydroxide pellets were in contact with carbon disulfide for about 24 hr, a bright red solid formed on the surface of the pellets. Silber and Maurin[21] reported that a rose-colored anhydrous form was obtained when the yellow or orange hydrates were dried over phosphorous pentoxide. Spectra similar to those from preparations above were obtrained from solutions of the red solid. If the carbon disulfide was dried (phosphorus pentoxide) and the sodium hydroxide pellets were dried in an oven, the red solid did not form after 1 day's contact. Apparently water is necessary for the reaction to take place.[22]

(3) *Method of Yeoman*[23]. The procedure given by Yeoman was followed in which the product from the reaction of hydrogen sulfide and sodium ethylate is reacted with carbon disulfide. This method was not as convenient as the first method and was not used after it was found that no significant differences in spectra were observed.

Sodium Sulfide

ACS analytical grade sodium sulfide nonahydrate was analyzed for sulfide gravimetrically as cadmium sulfide: *Anal.* Calcd: 13.35%. Found: 13.33%.

Sodium Tetrathiocarbonate

Sodium tetrathiocarbonate was prepared by the reaction of sodium disulfide[23] and carbon disulfide in equimolar amounts using the procedure described for preparation of sodium trithiocarbonate.

UV Absorption Spectra

Spectra were obtained with a DK-1 Beckman spectrophotometer by procedures previously described.[3]

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