These equilibria and their equilibrium constants have not been presented here because there appears to be a hysteresis phenomenon over part of the region concerned. A detailed study of this hysteresis is being made, and the effects which it may have on the mechanism of this linear adsorption will be presented in a later publication.

Above 70% relative humidity there is a rapid increase in the water absorbed on the amino groups. This is believed to be a condensation of water molecules on water molecules previously absorbed on the amino groups. This seems plausible because approximately 2.5 moles of water per amino group are absorbed at 60% relative humidity. This amount would be sufficient to saturate the hydrogen-bonding capacity of the amino group if the first molecule absorbed remains associated with two amino groups.

Table III shows the fraction of the total water absorption of casein which occurs on the free amino groups at each humidity studied. Previous treatments of the water-absorption of proteins have associated the effect of the various polar groups with some particular portion of the curve.[6] Our data show that the strongly polar amino group has its effect in all portions of the absorption isotherm.

Acknowledgment.—The authors gratefully acknowledge the suggestions of C. Roland Eddy regarding the free energy and heat of surface adsorption.

Summary

A series of benzoylated caseins has been prepared with varying amounts of free amino groups. Water-absorption studies on these samples have made it possible to distinguish between water absorbed on amino groups and water absorbed on the remaining groups of the casein.

The first step in the binding of water by the amino groups of casein seems to be a sharing of one molecule of water between two amino groups below 6% relative humidity. The B.E.T. treatment of the data, however, indicates a monolayer of one water molecule per amino group.

The second step is a linear increase in absorbed water with increase in relative humidity. Equations are presented for this increase between 0 and 60% relative humidity.

The third step is a rapidly increasing amount of absorption with increase of relative humidity and appears to be a condensation of water on water molecules already attached to the amino groups.

From 24 to 33% (depending on the relative humidity) of the water absorbed by casein is absorbed by the amino groups.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WAYNE UNIVERSITY]

"Nitro Captax"—6-Nitro-2-mercaptobenzothiazole—as a Reagent for the Identification of Alkyl Halides[1]

BY HAROLD B. CUTTER AND HAROLD R. GOLDEN[1a]

In spite of the importance of the alkyl halides, there are few satisfactory reagents for their identification. Therefore, it seemed desirable to attempt to find a compound that would react with alkyl halides to yield crystalline derivatives. 6-Nitro-mercaptobenzothiazole is such a substance. It reacts readily with primary and secondary but not with tertiary-alkyl halides to yield 6-nitrobenzothiazole sulfides. These may be oxidized to the corresponding sulfones, thus affording two crystalline derivatives for the original alkyl halide.

Experimental

Preparation of 6-Nitro-2-mercaptobenzothiazole.—This compound has been prepared by Teppema and Sebrell[1b] by the direct nitration of Captax (2-mercaptobenzothiazole) by a mixture of sulfuric acid and fuming nitric acid. We have found that a somewhat better method is by the nitration of "Altax" (benzothiazole disulfide) by means of nitric–sulfuric acid mixture, and reduction of the dinitrobenzothiazole disulfide by means of alkaline sodium sulfite.

50 g. of Altax (benzothiazole disulfide)[2] is dissolved in 250 g. (135 ml.) of concentrated sulfuric acid. The lumps are broken up and the mixture well stirred to assist solution. Since considerable heat is evolved by the dissolving of the Altax, the solution must be cooled before beginning the nitration. A mixture of 40 g. (25 ml.) of fuming nitric acid and 55 g. (30 ml.) of concentrated sulfuric acid is slowly added with constant stirring to the cooled reaction mixture. The temperature is not allowed to rise above 50°. After all the acid is added, the solution is stirred at room temperature for thirty minutes or more. The solution is then poured with stirring into 3 liters of ice water, filtered, washed well with water, and the wet cake of dinitrobenzothiazole disulfide suspended in 500 ml. of water. By stirring this suspension with a solution of 40 g. of sodium sulfite (anhydrous) and 20 g. of sodium hydroxide in 450 ml. of water, the disulfide is reduced and brought into solution as the sodium mercaptide. The deep red solution thus obtained is filtered, and poured into 3000 ml. of boiling 5% hydrochloric acid to precipitate the free mercaptan. It is necessary to acidify the solution in this manner in order to obtain a filterable precipitate. The mercaptan is then filtered, washed, and dried as thoroughly as possible on the filter. The nitromercaptobenzothiazole

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[1] Extract from a thesis presented by Harold R. Golden to the Graduate School of Wayne University in partial fulfilment of the requirements for the degree of Master of Science.

[1a] Present address: U. S. Rubber Company, Detroit, Mich.

[1b] Teppema and Sebrell, THIS JOURNAL, **49**, 1779–1785 (1927).

[2] The Altax used in these experiments was the Naugatuck Chemical Company product. Different batches varied slightly in melting points, but most samples melted in the range 173–175°. The Captax was prepared by the same company; it was about 95% pure and melted 170–173°.

TABLE I

Halide used	Alkyl 6-nitrobenzothiazolyl sulfides						Alkyl 6-nitrobenzothiazolyl-2-sulfones					
			Sulfur, %						Sulfur, %			
	M. p., °C.^{a}	Formula	Calcd.	Found from Cl	Found from Br	Found from I	M. p., °C.^{a}	Formula	Calcd.	Found from Cl	Found from Br	Found from I
Methyl	134	$C_8H_6N_2S_2O_2$	28.3			28.2	186^{b,g}	$C_8H_6N_2S_2O_4$	24.82			24.80
Ethyl	103–104	$C_9H_8N_2S_2O_2$	26.68		26.51	26.37	160^{b}	$C_9H_8N_2S_2O_4$	23.54		23.42	23.52
n-Propyl	94–95	$C_{10}H_{10}N_2S_2O_2$	25.21	25.09	25.10	25.02	181	$C_{10}H_{10}N_2S_2O_4$	22.39	22.08	22.30	22.35
i-Propyl	75–76	$C_{10}H_{10}N_2S_2O_2$	25.21	24.89	24.67	24.93	154^{e}	$C_{10}H_{10}N_2S_2O_4$	22.39	22.00	22.20	22.13
n-Butyl	64–65^{c}	$C_{11}H_{12}N_2S_2O_2$	23.89	23.49	23.80	23.69	152^{e}	$C_{11}H_{12}N_2S_2O_4$	21.34	21.09	21.11	21.40
i-Butyl	68–69^{c}	$C_{11}H_{12}N_2S_2O_2$	23.89	23.76	23.55	23.48	124^{f}	$C_{11}H_{12}N_2S_2O_4$	21.34	21.30	21.06	20.89
s-Butyl	oil						121^{f}	$C_{11}H_{12}N_2S_2O_4$	21.34	21.30	21.20	21.19
n-Amyl	48–49	$C_{12}H_{14}N_2S_2O_2$	22.70	22.35	22.46	22.31	125^{f}	$C_{12}H_{14}N_2S_2O_4$	20.39	20.18	20.03	20.08
i-Amyl	56–57^{d}	$C_{12}H_{14}N_2S_2O_2$	22.70	22.35	22.29	22.54	115	$C_{12}H_{14}N_2S_2O_4$	20.39	20.10	20.01	20.09
n-Hexyl	55.5^{d}	$C_{13}H_{16}N_2S_2O_2$	21.63		21.42		111.5	$C_{13}H_{16}N_2S_2O_4$	19.52		19.19	
n-Heptyl	39.5	$C_{14}H_{18}N_2S_2O_2$	20.65		20.23		123.5^{f}	$C_{14}H_{18}N_2S_2O_4$	18.72		18.35	
Allyl	72–73	$C_{10}H_8N_2S_2O_2$	25.41		25.09		No deriv.					
Benzyl	114–115	$C_{14}H_{10}N_2S_2O_2$	21.20	20.80			194	$C_{14}H_{10}N_2S_2O_4$	19.16	18.79		
Cyclohexyl	100–101	$C_{13}H_{14}N_2S_2O_2$	21.78		21.41		189 g.	$C_{13}H_{14}N_2S_2O_4$	19.64		19.04	

[a] All melting points were taken using a standardized thermometer calibrated for immersion. [b] The methyl and ethyl derivatives are more soluble than the others. Avoid using a large exess of acetic acid in these cases. [c,d,e,f,g] These derivatives melt rather closely together. However, in every case mixtures showed lowering of the melting point.

tends to retain several times its weight of water, and must be dried further before crystallization is possible. This is best accomplished by co-distillation with toluene rather than by heating in an oven. The dried mercaptan is then crystallized from glacial acetic acid. In order to obtain a satisfactory yield, it is necessary to re-use the saturated acetic acid filtrates from the crystallization. The impure mercaptan is extracted with a liter of boiling acetic acid, the solution is boiled with a few grams of Norite, and filtered while hot. As the solution cools, the nitromercaptobenzothiazole crystallizes in light yellow needles. These are then filtered off, washed with ether, and the acetic acid filtrate used to crystallize more mercaptan. Four such extractions are required to obtain 45 g. of 6-nitro-mercaptobenzothiazole, m. p. 252–254° (75% yield).

Preparation of 6-Nitro-benzothiazole Alkyl Sulfides.—Five-thousandths of a mole (1.06 g.) of 6-nitro-2-mercaptobenzothiazole is dissolved in a mixture of 10 ml. of butyl carbitol and 2.5 ml. of 2 *N* sodium hydroxide. 0.005 mole of alkyl halide is then added. If the alkyl halide is a chloride, 0.005 mole of potassium iodide (0.80 g.) is also added to the solution. The mixture is then heated under reflux for fifteen minutes for straight chain alkyl iodides, thirty minutes for bromides, and sixty minutes for chlorides. In the case of secondary alkyl halides and branched chain compounds, the time of refluxing should be doubled for the corresponding halide. When the refluxing is completed the mixture is cooled to room temperature and poured into 50 ml. of ice water. The derivative will usually solidify under these conditions. If, however, the compound remains an oil, it should be left in an ice-bath until it does solidify. The solid sulfide derivative is then filtered off and washed with dilute sodium hydroxide and water until the filtrate is no longer colored. The crude product is dissolved in methanol and boiled for a minute with a little Norite. The hot solution is filtered and cooled and the crystalline sulfide is removed by filtration.

Tertiary alkyl halides do not react to give derivatives.

Table I gives the melting points for fourteen common alkyl halides.

Oxidation of 6-Nitro-benzothiazole Alkyl Sulfides to the Corresponding Sulfones.—The oxidation is carried out according to the method of Bost, Turner and Norton.[3] One-hundredth of a mole of 6-nitro-benzothiazole alkyl sulfide is dissolved in glacial acetic acid. About 50 ml. of solvent is required for each gram of sulfide. In some cases it is necessary to warm the solution. A fifty per cent. excess of 7.5% potassium permanganate solution (40 ml.) is run into the sulfide solution. The progress of the reaction may be followed by spotting on filter paper. The manganese oxide color obscures observation in the flask. An excess does no harm. If the sulfide comes out of solution during the addition of the permanganate enough acetic acid should be added to keep the sulfide in solution; however, a large excess of solvent is to be avoided. The manganese dioxide and excess potassium permanganate are reduced by adding enough sulfurous acid to clear the solution. The sulfones are then completely precipitated by adding ice water to the solution. The derivatives are filtered, washed, dried, and purified by recrystallization from dilute ethyl alcohol.

The results for fourteen common alkyl halides are given in Table I.

Summary

6-Nitro-2-mercaptobenzothiazole—"Nitro Captax"—dissolved in butyl carbitol and treated with the calculated quantity of sodium hydroxide will react with primary or secondary, but not tertiary, alkyl chlorides, bromides or iodides, to form the corresponding sulfides. These are well crystallized compounds, but in some cases the melting points are rather low. They can easily be oxidized to the sulfones, which are higher melting compounds, somewhat easier to crystallize.

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[3] Bost, Turner and Norton, THIS JOURNAL, **54**, 1985 (1937).