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Chloramine-T as a Potential Scrubbing Agent: Removal of Odorous Sulfur-Containing Environmental Pollutants

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Pollution of air and water by odorous effluents from various industrial processes tends to be one of the most frequent sources of environmental pollution complaints. In recent years the number of complaints about disagreeable odors has approached the total of all other air pollution complaints received by U.S. authorities (CHEREMISINOFF & YOUNG 1975). There are well-known adverse social and economic effects of unpleasant odors. The former effects include interference with everyday activities and feelings of annoyance on the part of exposed persons, while the latter effects include the reduction in property values, and decrease in industrial productivity. Thioamides, sulfhydryl and other sulfur-containing compounds, are especially malodorous; they are derived from numerous industrial as well as biological sources and, thus contribute considerably to environmental pollution. As these thio compounds are malodorous, it would be advantageous to employ a suitable scrubbing liquid or sorbent for their removal from stack gases or wastewater effluent. Thioacetamide has also been reported to be toxic and carcinogenic to livers of rats when they are fed daily with the compound for six months (REES et al. 1966). Scrubbing with an appropriate agent would then also remove this probable carcinogenic agent, i.e., thioamide from stack effluent. Hypochlorite has been used as a scrubbing agent (SAWYER 1957) because of its strong, oxidative and chlorinating abilities. However, it has the disadvantage of instability, decomposing rapidly in the presence of light (ALLMAND et al. 1925; SIDGWICK 1962). Chloramine-T has been suggested as an alternative scrubbing agent for the removal of odorous aromatic amine environmental pollutants (TRIEFF & RAMANUJAM 1977).

The present investigation concerns the reaction with Chloramine-T of two thioamides and three thiols which may be emitted as industrial air and water pollutants. The main basis for this study was that an oxidimetric reagent such as Chloramine-T ($p\text{-}H_3C\text{-}C_6H_4SO_2NCl\ Na{\cdot}3H_2O$; CAT) which is also used as a disinfectant, antiseptic, deodorant, etc. (GUTMAN 1941) might function as effectively as hypochlorite in terms of odor removal and yet have an enhanced stability. This communication consists of the results of preliminary experiments done in our laboratory using the sensory approach (AMOORE 1970), without the use of a scrubber or flow system. The results of the study suggest that

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CAT solution would be an effective scrubbing liquid for malodorous thioamide and thiol environmental pollutants.

MATERIALS AND METHODS

Materials: Thioacetamide (TAA) (99.6% purity), thiobenzamide (TBA) (96% purity), thiobenzoic acid (TBZA) (95% purity), thiophenol (TP) (97% purity) and ethanethiol (ET) (97% purity), were of analytical reagent grade and were not further purified. CAT was freed from possible dichloro contaminant by washing it several times with carbon tetrachloride and dried in a vacuum desiccator over $CaCl_2$ (HIGUCHI et al. 1967).

Methods: The reaction mixture containing excess of CAT compared to the thioamide or thiol (sulfur compound: CAT≈1:4 in milli moles) was prepared in 50% aqueous ethylene glycol (v/v). The reaction for thioamides is instantaneous and the reaction mixture contains the oxidation products such as organic acid, ammonium sulfate, sulfur, sodium chloride and p-toluene sulfonamide (GOWDA et al. 1979), while for the thiol, the reaction mixture contains sulfate, aldehyde, sodium chloride and p-toluene sulfonamide (MAHADEVAPPA & GOWDA 1975).

A standard method of determination of odor threshold was used as described by AMOORE(1970). Solutions of different concentrations (successive binary dilutions) of each sulfur compound ranging from 31.25 to 4000 ppm for each thioamide and from 7.81 to 125 ppm for each thiol were prepared by dissolving the compound in 50% aqueous ethylene glycol. In the same way, similar solutions of the sulfur compound with excess of CAT were prepared. For each concentration, there were two samples containing odorant and three containing only 50% aqueous ethylene glycol (blanks). Odorous solutions and blanks consisted of 20 mL samples placed in 32 mL stoppered brown bottles. Each member of the odor panel consisting of ten untrained individuals was presented with a set of five bottles at each dilution, and asked to determine which were the two odorous bottles. Each panel member was also requested to ignore the chlorine smell due to the unconsumed CAT present in the reaction mixture and concentrate only on the mercaptan odor of the compound. The odor threshold for each panel member was the lowest concentration below which detection errors were made. The median odor threshold concentration for the panel was the dilution at which only 50% of the panel could detect the odor (CHEREMISINOFF & YOUNG 1975).

RESULTS AND DISCUSSION

The results of the odor analyses of TAA, TBA, TBZA, TP and ET and their respective reaction products are shown in Tables 1 and 2. Table 1 consists of the individual value of the odor threshold of the panels (the constitution of the panels were

TABLE 1

Odor Thresholds of Thioacetamide, Thiobenzamide, Thiobenzoic Acid, Thiophenol and Ethanethiol and Their Reaction Products

Subject*	Odor Threshold Level (ppm)									
	Panel 1				Panel 2					
	TAA	TAA+ CAT	TBA	TBA+ CAT	TBZA	TBZA +CAT	TP	TP+ CAT	ET	ET+ CAT
1	62.5	125.0	1000.0	4000.0	31.3	>125.0	31.3	>125.0	7.8	>125.0
2	62.5	4000.0	250.0	4000.0	31.3	>125.0	<7.8	125.0	<7.8	>125.0
3	250.0	125.0	250.0	250.0	<7.8	>125.0	<7.8	>125.0	<7.8	>125.0
4	62.5	125.0	500.0	2000.0	31.3	>125.0	31.3	>125.0	<7.8	>125.0
5	125.0	250.0	500.0	4000.0	31.3	>125.0	<7.8	>125.0	<7.8	>125.0
6	250.0	1000.0	1000.0	4000.0	31.3	>125.0	<7.8	>125.0	<7.8	>125.0
7	250.0	4000.0	500.0	4000.0	<7.8	>125.0	<7.8	125.0	<7.8	>125.0
8	125.0	2000.0	4000.0	4000.0	31.3	>125.0	31.3	>125.0	<7.8	>125.0
9	125.0	2000.0	1000.0	2000.0	31.3	>125.0	31.3	>125.0	<7.8	>125.0
10	250.0	62.5	250.0	2000.0	31.3	<7.8	<7.8	15.6	<7.8	>125.0

*The subject number is for convenience; different panels were used for testing the thioamides and reaction mixtures (Panel 1) and thiols and reaction mixtures (Panel 2).

TABLE 2

Median Thresholds of Odor Panels for Thioacetamide, Thiobenzamide, Thiobenzoic Acid, Thiophenol and Ethanethiol and Reaction Mixtures

Compound	Median Odor Threshold Level (ppm)		Ratio
	I Compound	II Reaction Mixture	II / I
Thioacetamide (TAA)	94.7	406.1	4.29
Thiobenzamide (TBA)	406.1	4000.0	9.85
Thiobenzoic acid (TBZA)	20.6	>125.0	>6.07
Thiophenol (TP)	13.1	>125.0	>9.54
Ethanethiol (ET)	<7.8	>125.0	>16.03

somewhat different for the thioamides and the thiols) while Table 2 gives the median odor threshold values of the panels, calculated by plotting a graph of number of subjects (ordinate) against number of binary dilution, i.e., 0, 1, 2, 3--(abscissa). The value of the binary dilution corresponding to the ordinate value 5 (1/2 the panel) is the median odor threshold in binary dilution units (n). Where no members detected the highest concentration of reaction mixture the median value was denoted as being greater than that concentration. The actual median odor threshold concentration equals $4000/2^n$ and $125/2^n$ for the thioamide and the thiol respectively. It is evident from the Tables that in each case the odor threshold of the sulfur compound is several times smaller than that of the corresponding reaction mixture containing CAT and oxidation products. Thus, with TAA, for example, the median threshold level is 94.7 ppm. while that of its reaction mixture is 406.1 ppm (ratio of 4.29), the reaction mixture thus showing a significantly higher odor threshold. In the case of TBA the ratio is greater (>9.85) and that in the case of ethanethiol is even greater (>16.03).

No doubt the scattering of results for olfactory threshold would have been diminished if the entire panel could ignore odors other than mercaptan odors. Some members were particularly sensitive to the odors of acetic acid and NH_3, the products (and/or the by-product, acetamide) of the TAA reaction; others could not ignore the chlorine odor of CAT.

The reaction between CAT and thioamide is extremely rapid and stoichiometric in pH 1 buffer or 0.1N H_2SO_4 medium (GOWDA et al. 1979), while the reaction of CAT with thiols is fast in acid medium and stoichiometric at a definite pH (MAHADEVAPPA & GOWDA 1975). CAT has a number of other advantages over HOCl in that it is substantially more stable and can be stored both prior to scrubbing and after the scrubbing operations, and would not decompose to any considerable degree. Finally, it converts the carcinogenic TAA and TBA into non-carcinogenic substances. Consequently, CAT has an excellent potential for being employed as a scrubbing liquid.

CONCLUSION

A detailed study of the reaction of thioacetamide, thiobenzamide, thiobenzoic acid, thiophenol and ethanethiol (emitted from industrial stacks or as industrial wastewater effluents and ultimately becoming environmental pollutants) with Chloramine-T has been made. Odor studies based on the sensory approach, have been performed on the reactants as well as the reaction mixtures containing the oxidation products, using odor test panels to determine the odor threshold levels. In all cases the median odor threshold concentration has been raised substantially by reaction with CAT. From the preliminary studies it is concluded that this oxidative technique has potential application in air and water pollution odor control.

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