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Reactivity of Nitrogenous and Other Organic Compounds with Aqueous Chlorine

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Chlorine has been used to disinfect municipal water supplies in this country since 1908. Chlorine has become the primary drinking water disinfectant in the United States used to prevent the transmission of waterborne diseases. Free aqueous chlorine exists as hypochlorous acid (HOCl) and hypochlorite ion (OCl^-). These forms react readily with ammonia and other nitrogenous compounds to form combined chlorine and oxidation products. Although much research on chlorine and its mechanisms of reaction and disinfection efficiency has been accomplished (Morris 1980, 1965), information on reactions of chlorine and nitrogenous compounds at low concentrations is relatively limited. The amount of information developed over the last fifty years on the occurrence of nitrogenous compounds in water supplies has also been scarce. Recently, the U.S. Environmental Protection Agency has completed studies compiling findings of nitrogenous and other organics in water supplies.

With the exception of amino acids, no other group of nitrogen containing organic compounds (N-compounds) has been thoroughly investigated as to its reaction with chlorine. In a recent study by Morris (1980), some 26 N-compounds were treated with chlorine to determine their reactivities. However, the test concentrations varied, and no standard protocol was used. Other studies have detailed the reactions of organics with chlorine, but no standard protocol or concentrations were observed, and therefore studies are difficult to compare (Jolley 1975, Pereira 1973, Wilkens 1979, Shimizu 1973, Barnhart, 1972, McCarty 1980, Youssefi 1978). It was to this end that this study was initiated to investigate reactivities with chlorine of specific N-organics compounds in various classes in a standard protocol. In addition to information gathered as to what will or will not react with aqueous chlorine, another most important facet is the time factor. If in the water treatment disinfection process the chlorine and organic compound are reacted completely in 30-60 minutes, then the organic will no longer exert a demand. Thus, the residual sent out of the disinfection stage will be a true residual, available to destroy harmful microorganisms. If, in fact, the organic-nitrogen compound does not react at all, over a long (one week) period, then with respect to chlorine demand, the compound also will present no problem.

However, it is the intermediate one day or greater reactivity period that may present a chlorine demand problem which could have health implications. Slowly or moderately reactive compounds are not fully reacted in the treatment process, and can be further reacted with the chlorine residual once in the water transmission lines. Thus, an apparently safe chlorine residual is actually subject to dissipation. In addition to any chlorine demand aspects of the test compounds, decomposition products from oxidation reactions that do not produce combined chlorine may continue to exert free chlorine demand. The reactivity of certain functional groups towards free chlorine should be considered. Compounds selected were drawn mainly from the Distribution Register of Organic Pollutants in Water (1973) list and the Priority Pollutants (1978) list and represent a mix of naturally occurring organics and synthetic chemicals introduced into the environment (Lytle 1981).

MATERIALS AND METHODS

Over two hundred organic compounds were obtained in the purest form available commercially. These compounds were dissolved in 0.05 M phosphate buffered water at pH 6.0, 7.0 and 8.0. This concentration of buffer provided the minimum amount of buffering required to maintain pH stability. Buffer solutions were prepared using KH_2PO_4 and NaOH.

To the solutions or suspensions of the organic compounds, chlorine (HOCL) was added at organic compound to chlorine mole ratios of 1:0.5, 1:1, and 1:3. These correspond to chlorine concentrations of 0.6, 1.2, and 3.5 mg/L free chlorine, and are representative of concentrations used in drinking water disinfection. Because free chlorine is attacked by ultraviolet light, the reaction flasks were stored, when not being analyzed, in a light tight cabinet at 25°C. At intervals of sixty minutes, one day, three days, and seven days, samples were removed from the reaction flask for analysis. To determine the extent of chlorine reaction or chlorine demand of the system, the residual chlorine was measured by amperometric titration (Wallace and Tiernan amperometer, Model A-790). With each set of samples, a control sample made up to 1.0 mg/L free chlorine was also examined.

The amperometric titration procedure for the measurement of free chlorine is described in Standard Methods, Part IV 408C, Chlorine Residual (1980). All samples were weighed out to the nearest 0.1 milligram. Solutions were made up with ultra pure Super Q® Water (Milli-Q-Reagent Grade Water System). Stock solutions of chlorine were made up from commercial hypochlorite (Clorox®) solutions, diluted, and standardized with the amperometer. After the experiments were completed, four categories of reactivity were established. The criteria were as follows: 1. All compounds reacting with chlorine with a 90% or greater chlorine demand in one hour were classified as very reactive (VR). 2. Compounds reacting to give a 90% chlorine demand within 1-3 days were designated as moderately reactive (MR).

3. Compounds reacting to give a 90% chlorine demand in one week were designated as slowly reactive (SR). 4. Compounds displaying no chlorine demand or very little were labeled as non-reactive NR or very slightly reactive (VSR).

RESULTS AND DISCUSSION

In approximately 90% of all cases, no effect or only very slight effects of pH on chlorine concentrations in the establishment of reactivity categories, was noted. Therefore, no distinction among these differing reaction conditions has been made in the summary of the data presented in Table I with respect to pH.

Although there is no substitution for the actual compendium of individual compounds, some generalizations have been derived from these studies. By use of these generalizations, some predictability as to chlorine reactivity of compounds similar to those listed in Table 1 can be deduced.

Amino acids, phenolics, organic sulfur compounds, pyrroles, prolines and indoles were very reactive. Imide structures were moderately reactive and indole structures generally were very reactive. Xanthines varied depending upon other functional groupings in the structure. Thus, with amino group constituents, xanthines were very reactive, otherwise most of these structures were slowly reactive to non-reactive. Other compounds tested showed little or no reactivity as measured by these tests. Thus, alcohols, nitroso compounds, pyridines, aldehydes, ketones, carboxylic acids, ether structures and quinolines were non-reactive. Amide structures were nonreactive except when an organic sulfur compound was present. Amino structures vary depending upon the type of bonding involved. VR, MR, and SR categories were observed in tertiary amine structures. Secondary amines were generally MR and primary amines generally were VR. Purine compounds varied from NR-VR. Alkane and other straight chains were NR. Naphthalenes and chlorinated hydrocarbons were also NR.

Some compounds are repeated when listed under various functional categories, however, this is done for ease of classification in that two functional groups may be on the same model compound and they could either enhance or retard the reactivity. The twenty-six nitrogenous compounds used by Morris were tested and the results were substantially the same as in this study. Morris' review (1975) indicates rapid reactivity of humics, amino acids and phenols, slower reactivity of amides and imides, and a less readily occuring reaction with hydrocarbons than shown in this study. Morris (1965) also demonstrated rapid amine reactions but at different conditions than used in this investigation.

The generalizations concluded in this study have basically been in agreement with the other studies reported in the literature. Jolley's work (1975) with xanthines, phenols, pyrimidines and purines, Pereira's work (1973) with amino acid, Wilken's work

Table 1. Chlorine Reactivity Characteristics of Organic Compounds

Compound	Reactivity Category VR	MR	SR-NR
Phenolics			
m-Aminophenol	X		
Bromocresol Purple (sulfonic acid)	X		
Caffeic Acid	X		
Ferulic Acid	X		
Gallic Acid	X		
Gentisic Acid	X		
2,4 Dihydroxybenzoic Acid		X	
3,5 Dimethylphenol	X		
3,4 Dimethylphenol	X		
2,6 Dimethylphenol	X		
Humic Acid (others)		X	
p-Hydroxybenzaladehyde	X		
p-Hydroxybenzoic Acid	X		
p-Hydroxycinnamic Acid	X		
Methyl Salicylate	X		
O-Nitrophenol		X	
P-Nitrophenol		X	
Pentachlorophenol		X	
Phenol	X		
Protocatechuic Acid	X		
Resorcinol	X		
Syringaldehyde	X		
Tannic Acid	X		
Tyrosine (amino acid)	X		
Vanillic Acid	X		
Vanillin	X		
Chlorinated Hydrocarbons-Pesticides			
Aldrin			X
Aroclor 1016			X
Aroclor 1254			X
Chlordane			X
Chlorobenzene			X
DDD			X
DDE			X
DDT			X
Dieldrin			X
Endrin			X
Hepthachlor			X
Lindane			X
Methyoxychlor			X

Compound	Reactivity Category VR	MR	SR-NR
Aliphatics			
Acrylonitrile (nitrile)			X
Acetone			X
Butyric Acid			X
Carbinol			X
Citric Acid			X
Cyclopentane (cyclic)			X
Epichlorohydrin			X
b-2-Furylacrylic Acid			X
"Grease" -(Freon-Hex) glycol			X
Glycolic Acid			X
Glycerin			X
Hexadecane			X
Hexanol			X
Isophorone			X
Kerosene (aromatics)			X
L.A.S.			X
Maleic Acid			X
Octane			X
Paraffin Oil			X
Petrol Hydrocarbons			X
Pentane			X
Sodium Tartrate			X
6-Undecanone			X
Indoles			
Brucine (pyrrole)		X	
5-Hydroxyindole		X	
Indican		X	
Indole			X
Indole Acetic Acid		X	
3-Indole Butyric Acid		X	
3-Indole Propionic Acid		X	
Skatol		X	
Tryptophan (Amino Acid)		X	
Lactone or Sugars			
Ascorbic Acid		X	
Indican (indole)		X	
Dextrose			X
Tannic Acid (phenol)		X	

Table 1. Chlorine Reactivity Characteristics of Organic Compounds (Cont'd)

Compound	Reactivity Category		
	VR	MR	SR-NR
Amides			
Hippuric Acid			X
Maleamic Acid			X
Naphthalene Acetamide			X
Saccharin			X
Toluenesulfonamide (organic sulfur)		X	
Quinolines			
2,6 - Dimethylquinoline			X
Hydroquinone		X	
8 - Methylquinoline			X
0 - Phenanthroline			X
Quinoline			X
Imides			
Creatinine		X	
Histidine (Amino Acid)	X		
Maleimide	X		
Succinimide		X	
Urea		X	
Nitroso			
N-Nitrosodimethylamine		X	
Nitrosophenylamine		X	
Pyrimidine			
Barbituric Acid	X		
Cytosine		X	
Folic Acid (Amino Acid)	X		
Pyrimidine			X
Thymine		X	
Uracil		X	
Uracil, -5 Chloro		X	

Compound	Reactivity Category		
	VR	MR	SR-NR
Amines			
Adenine		X	
4-Aminoantipyrine	X		
m-Aminophenyl	X		
Aminephenylnapthol		X	
Aniline	X		
Barbituric Acid	X		
Benzidine (SO_4)	X		
Benzyl Adenine		X	
Betain (salt)	X		
Brilliant Green (salt)	X		
3,3'-Dichl'benzidine			X
Dimethylamine - HCl		X	
Diphenylhydrazine (hydrazine)			X
E.D.T.A.	X		
Guanine	X		
Hydroxylamine-HCl	X		
Leuco-Crystal Violet			X
Lecithin (glyceride)	X		
Methyl Amine		X	
Methylene Blue			
p-Nitrosodiphenylamine (nitroso)		X	
Rhodamine B		X	
Sulfamic Acid	X		
P-Toluidine	X		
Trimethylamine - HCl	X		
Tris (hydroxymethyl) aminomethane	X		
Pyrrole Compounds			
2-Acetylpyrrole		X	
Brucine (indole)	X		
Carbazole		X	
N-Methylpyrrole		X	
Nicotine		X	
3-Pyrroline		X	
Pyrrole		X	
Saccharine			X

Table 1. Chlorine Reactivity Characteristics of Organic Compounds (Cont'd)

Compound: Amino Acids	Reactivity Category: VR	MR	SR-NR	Compound: Aromatics Misc.	Reactivity Category: VR	MR	SR-NR
Arginine	X			Benzoic Acid			X
Alanine		X		Biphenyl			X
Aspartic Acid	X			Butylbenzylphthalate			X
Casein (polymer)		X		Cyanuric Acid			X
Cystine	X			Dibutylphthalate			X
Creatine		X		Dichlorobenzidine			X
Folic Acid	X			Di-chlorophenoxy			X
Gelatin		X		Acetic Acid			
Glutamic Acid		X		Diethylphthalate			X
Glutathione	X			Dimethylbenzaldehyde			X
Glycine	X			Dimethylphthalate			X
Glutamine	X			Dioctylphthalate			X
Glycylglycine	X			Diphenylhydrazine			X
Histidine	X			Kerosene (aromatics)		X	
Hydroxyproline	X			p-Methoxycinnamic Acid			X
Isoleucine	X			Pyrene			X
d,l Leucine	X			Potassium hydphthate			X
Lysine	X			2-Pinene (bicyclo)			X
Methionine	X			Stilbine			X
Nucleic Acid (purine)	X			Syringaldazine			X
Ornithine	X			Xylenes			X
Proline	X						
Phenylalanine	X			**Polynuclear Aromatics**			
Sarcosine	X						
Serine	X			Anthracene			X
Taurine	X			Chrysene			X
Threonine	X			Fluoranthene			X
Thyroxine			X	Fluorene			X
Tryptophan	X			1-Napthaleneacetamide			X
Tyrosine (phenol)	X			1-Napthaleneacetic acid			X
Valine	X			2-Naphthoxyacetic acid		X	
Phenoxy Acid - Herbicides				**Pyridines**			
2,4 D			X	3-Chloropyridine			X
2,4,5 TP			X	2,4,6 - Collidine			X
				Nicotinic Acid			X
				Phenanthroline			X
				Piperdine			X
				Piperdine - HCL		X	
				Pyridine	X		

(1979) with benzene, PCBS, chlorinated hydrocarbon, and polycyclics, and Newell's studies (1976) with ketones, acids, aldehydes, and humics (1973) agree with this study. The EPA Chlorination of Organics Report (Stevens, 1975), Hoyuano's report with purines, and Shimizu work (1973) with water plant phenols fit well with the results obtained with our results using the standard protocol. The National Academy of Science Report (1979), Christman's work (1975) with humics, Barnhart's work (1972) with benzene, acids, alcohols, phenols, and cresols, and McCarty's work (1980) on phthalates, naphthalenes, and chlorobenzenes also corresponded to our results. Other studies such as Youssefi's work (1979) with tannic, vanillic and gallic acids, Kimberle's work (1979) with LAS, and Katz's study (1971) with NTA were compared favorably with this report.

The above discussion indicates that other reports have supported our generalizations in the main and in cases where they did not, other reaction times and concentrations were used. This demonstrated the need for a standard protocol for chlorine reactivity. In this study, a molar ratio of 3:1 was selected as it corresponds to 3.5 mg/L chlorine. This approximates what might be a typical chlorination dosage in practice. Compound concentrations of 1.2 mg/L were used as a "worst" case example of chemicals in water sources.

In summary, a protocol has been proposed for the testing and systematic classification of organic compounds as to their reactivity to chlorine. The ratios and concentrations are such that we could expect to occur in water treatment. By use of the generalizations formulated, some predictions as to reactions of organics in the chlorination process can be derived.

Thus, an important thrust of this study is that the compounds tested can serve as models for treatability problems that may confront utilities.

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