Trattamento dell'acqua

6.1. Introduzione

I tipi di trattamento dell'acqua possono essere tre:

a) Purificazione per uso domestico

b) Trattamento per applicazioni industriali specializzate

c) Trattamento di acque reflue per renderle accettabili per il riutilizzo.

Il tipo ed il grado dei trattamenti da usare in ciascuna di queste direzioni sono fortemente legati alla fonte ed all'uso dell'acqua. Ad esempio, la sterilità e la mancanza di virus è centrale nella potabilizzazione dell'acqua, la durezza deve essere bassa se l'acqua verrà usata in un impianto di riscaldamento. Le specifiche per scaricare l'acqua nell'ambiente sono molto severe e sono regolate dalla legge, mentre quelle per il riutilizzo sono variabili caso per caso.

6.2 La potabilizzazione dell'acqua

La potabilizzazione di un'acqua di falda, o di un'acqua di fiume o di lago, viene effettuata in impianti pluristadio le cui caratteristiche possono essere diverse a seconda delle caratteristiche dell'acqua da trattare. La figura 6.1 rappresenta uno schema tipo per questi impianti.

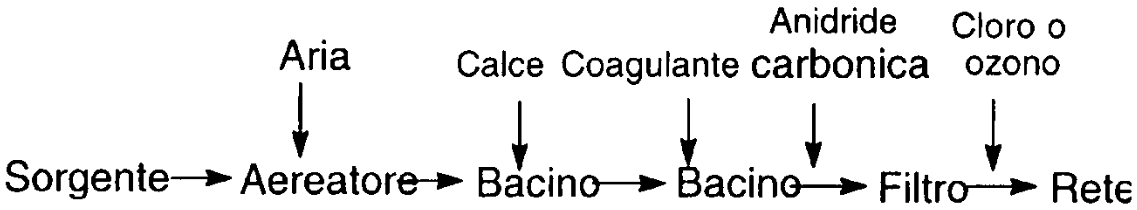
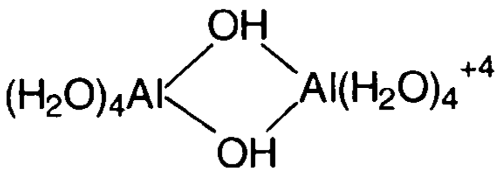


Figura 6.1. Schema a blocchi di un impianto di potabilizzazione dell'acqua

L'acqua viene pompata in un aereatore. Soluti volatili come anidride carbonica, idrogeno solforato, metano, piccoli composti cloroorganici ecc. vengono così trasportati dal flusso d'aria nell'atmosfera. Spesso questa operazione riduce anche la concentrazione di composti odorosi. Se vi sono composti facilmente ossidabili, quali ad esempio il Fe^{2+}, questi vengono ossidati, a dare, ad esempio il Fe^{3+}, che precipita. Nel secondo stadio viene eliminata la durezza, addizionando calce [$Ca(OH)_2$]. Si separano così i carbonati di calcio e di magnesio. L'acqua alcalina per l'eccesso di calce e torbida per la presenza di questi precipitati viene immessa in un bacino di sedimentazione, aggiungendo dei flocculanti per aumentare l'efficienza della separazione dei precipitati. I flocculanti sono, ad esempio, $Fe_2(SO_4)_3$, $Al_2(SO_4)_3$ 18 H_2O, che, nell'ambiente alcalino, formano i rispettivi idrossidi, insolubili e gelatinosi. Il fiocco di precipitato occluderà i materiali solidi sospesi. Inoltre, si formeranno delle specie cationiche a ponte che interagiranno specificamente con le particelle colloidali inducendo la coagulazione.



Il $Fe_2(SO_4)_3$ ha il vantaggio di operare a pH 4-11. Allo stesso scopo si usano a volte la silice, SiO_2, o $Fe(SO_4)$ 7 H_2O in presenza di aria a pH 9; $FeCl_3$; il policloruro di alluminio $Al(OH)_xCl_y$, amido, cellulosa, materiali proteici, polisaccaridi, o, più recentemente, polimeri sintetici come poliacrilamidi.

Dopo la sedimentazione dei solidi, l'acqua è trattata con anidride carbonica, per rimuovere l'eccesso di calce. Si ottiene ancora un precipitato di carbonato di calcio, e si lascia tornare il pH alla neutralità. L'acqua è quindi disinfettata per trattamento con cloro o con ozono, filtrata su sabbia o carbone attivo ed immessa nella rete. I solidi ottenuti sono raccolti ed avviati in discarica.

2. Natural Waters

The earth is unique in having a significant (ca. 70%) surface covering of liquid water. Table 1.7 summarizes the global distribution of surface and near-surface water. The oceans contain a very large majority of the terrestrial water; most of the remainder is glacial ice.

Almost all of the fresh liquid water is groundwater, with at least half of the total present at depths of greater than 1000 m. (Much less than 1% of the total is in the root zone of the soil.) Lakes and rivers, despite their extreme importance for humans, are a quantitatively insignificant component of the world's water supply. There is about as much water in the atmosphere as there is in all the world's rivers.

Evaporation and precipitation are in almost exact balance on a global basis. Of the rain and snow falling on land, about a third runs off and enters the ocean via river and lake drainage systems. The other two-thirds is retained temporarily by the

Table 1.7. Global Distribution of Water

	Volume (km^3)	%
Oceans	1.37×10^9	97.3
Ice caps, glaciers	3.0×10^7	2.1
Lakes	1.2×10^5	8×10^{-3}
Rivers	1.2×10^4	8×10^{-4}
Ground water	8.3×10^6	0.6
Soil moisture	2.5×10^4	1.8×10^{-3}
Atmosphere	1.3×10^4	9×10^{-4}
	1.41×10^9	100.0

soil and returned to the atmosphere directly (by evaporation) or indirectly (by transpiration from plants).

a. Water as Solvent and Reactant

Water is an angular molecule with an H–O–H bond angle of 104.5° and an O–H bond length of 0.96 Å. The energy of dissociation of the O–H bond is about 450 kJ/mol, much higher than that for typical C–C bonds which average around 350 kJ/mol.

Water has a very high latent heat of vaporization (2300 J/g, by far the highest of all common liquids), and accordingly, considerable energy must be supplied to the liquid to convert it to the vapor. Nevertheless, the atmosphere always contains water both in the vapor state and in the form of small aerosol droplets. At 20°C, up to 17 g water vapor/m^3 can be held in the air.

Liquid water. The structure of liquid water is still controversial. Some models suggest that it can be represented as a slightly disordered ice, although these representations do not account very well for the remarkable degree of supercooling (up to 40°C) that the liquid can exhibit. It would be expected that ice-like assemblages would be efficient nuclei for crystallization.

An early proposal by Pauling (1960) was that liquid water could be considered a self-clathrate (Figure 1.6), with a central, nonhydrogen-bonded "guest" molecule surrounded by a hydrogen-bonded framework of pentagonally and hexagonally-faced polyhedra. This model appears to be somewhat too "ordered" to account for many of the properties of water (Frank and Quist, 1961), but its central idea of a structure incorporating both "framework" (hydrogen-bonded) and "interstitial" (nonhydrogen-bonded) water molecules has been included in many of the more recent attempts to describe liquid water. The "flickering cluster" model (Nemethy and Scheraga, 1964) has many adherents; it posits the existence of compact, short-lived assemblages of hydrogen-bonded molecules in equilibrium with unassociated, "vapor-like" water. Cluster models can be expressed as an equilibrium between two

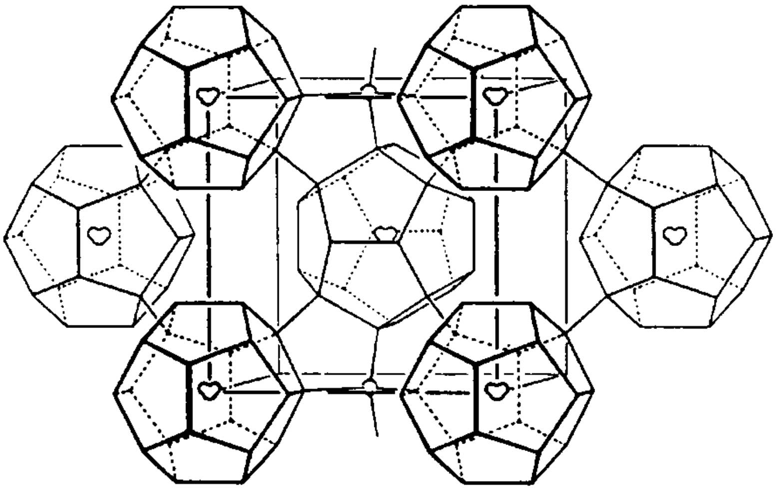


Figure 1.6. Pauling's host-guest model for liquid water structure. The central water molecule is envisioned as not taking part in hydrogen bonding with the surrounding icosahedral assemblage of 20 fully hydrogen-bonded molecules. From J. L. Kavanau (1964), *Water and Solute-Water Interactions*. Reprinted by permission of Holden-Day, Inc.

forms of water; "bulky" water $(H_2O)_b$ which is ice-like; that is, consisting of associated, open structures with considerable void space, and "dense" water $(H_2O)_d$ which is more closely packed and less hydrogen-bonded. Cooling such an assemblage would cause a shift in the equilibrium toward the bulky form, which would eventually crystallize, whereas heating it would increase the proportion of dense water which would escape as vapor.

Water as a solvent. Aqueous solutions can be thought of as rearrangements of the structure of liquid water in order to accommodate foreign molecules, which can interact with the solvent in more or less consequential ways. Two extremes can be imagined; a virtual noninteraction in which the water molecules merely circumvent the solute, arranging themselves around it; and an almost complete incorporation, in which the functional groups of the solute molecule placidly combine in the hydrogen-bonded lattice of the solvent. The former extreme is approximated in solutions of aliphatic hydrocarbons; the second, in solutions of sugars and sugar alcohols.

The molar solubility of aliphatic hydrocarbon gases in water shows a maximum at C_3–C_4. This appears to represent the optimum size for a clathrate-like structure in which the host water molecules arrange themselves around the guest hydrocarbon. This is a good example of the so-called "hydrophobic interaction" or "like-dissolves-like" phenomenon. Presumably, larger cages, such as would be required to surround a larger molecule, are less stable. The negative entropy change that occurs when a nonpolar gas is dissolved in water is quite considerable, suggesting that a more ordered, "ice-like" state results as the solute exerts a tendency for the water molecules in its vicinity to become more "bulky."

The properties of water in the presence of nonpolar solutes (those not having functional groups that can significantly interact with the water lattice) are to some degree similar to those of water containing nonpolar gases. Thus, for example, there is a roughly inverse linear relationship between the molar volume of a saturated hydrocarbon and its solubility. The aqueous solubilities of aliphatic hydrocarbons decrease sharply with increasing chain length, from about 5×10^{-4} M for *n*-pentane to 2.5×10^{-5} M for *n*-heptane and 1×10^{-7} M for *n*-dodecane (McAuliffe, 1966). It appears as if the formation of structured cavities having water molecules of sufficient size to accommodate hydrocarbons having more than a very few carbon atoms is energetically quite unfavorable.

Aromatic hydrocarbons also decrease in solubility with size, although they are far more soluble (approximately two orders of magnitude on a molar basis) than aliphatic hydrocarbons having the same number of carbon atoms (Mackay and Shiu, 1977; Pearlman et al., 1984). The solubilities of benzene, toluene, and naphthalene are, respectively, 1750 mg/L (0.022 M), 550 mg/L (6×10^{-3} M), and 32 mg/L (2.5×10^{-5} M). Even a rather large aromatic compound such as phenanthrene ($C_{14}H_{10}$) has a solubility of nearly 1μM. It is probable that there are significant charge-transfer interactions between water molecules and the pi electron clouds of aromatic species.

Striking increases in water solubility result when heteroatoms are introduced into hydrocarbon chains, due to the ability of the substituent to take part in hydrogen bonding and assume a position in the structural framework of the liquid. The solubility of *n*-hexane is only about 1×10^{-4} M, but that of di-*n*-propyl ether is about 2.5×10^{-2} M, and triethylamine is miscible with water. Introduction of polar or charged functional groups with exchangeable or ionizable hydrogens, such as -OH, -NH-, $-SO_3^-$, or $-COO^-$/-COOH, causes dramatic changes in solubility behavior; hydrophobic interactions become less important than the short-range, stronger interactions between the polar groups and water molecules, unless the polar group is contained in a molecule having extensive nonpolar regions (such as a long-chain alcohol). As an example, a short-chain alcohol such as *n*-butanol may participate in water clusters by forming up to three hydrogen bonds, using the hydrogen atom and two electron pairs on oxygen. The nonpolar end of the molecule is probably surrounded by a clathrate-like region similar to the solvation cages of *n*-alkanes. By analogy to hydrocarbons, aromatic -OH compounds (phenols) are much more soluble than the corresponding linear alcohols; the C_7 aliphatic alcohol *n*-heptanol has a solubility of 8×10^{-3} M, and the cresols (H_3C-Ph-OH) around 0.2 M.

As more OH groups are introduced into a molecule, its solubility characteristics depend to some extent on how well it fits into the framework of the structured component of water. It has been noted that the spacings between oxygen atoms of many very water-soluble compounds correspond rather closely to the first and second nearest-neighbor distances of the ice lattice (Berendsen, 1975). Seemingly minor changes in the stereochemistry of polyfunctional compounds often, however, lead to

Many naturally occurring substances as well as compounds of anthropogenic origin are amphiphilic; that is, contain a highly polar region and a nonpolar region. Fatty acids and synthetic detergents are straightforward examples of this class of compounds, but polymeric dissolved organic species such as humic substances (see Sections 1.B.1f and 1.B.3a) also display these characteristics (Wershaw, 1986; Yonebayashi and Hattori, 1987). At very low concentrations, these substances may exist in true solution, but as their concentrations increase, interactions among their hydrophobic portions become dominant, and they produce oligomeric aggregates which eventually form particles of colloidal dimensions, called micelles (Figure 1.7).

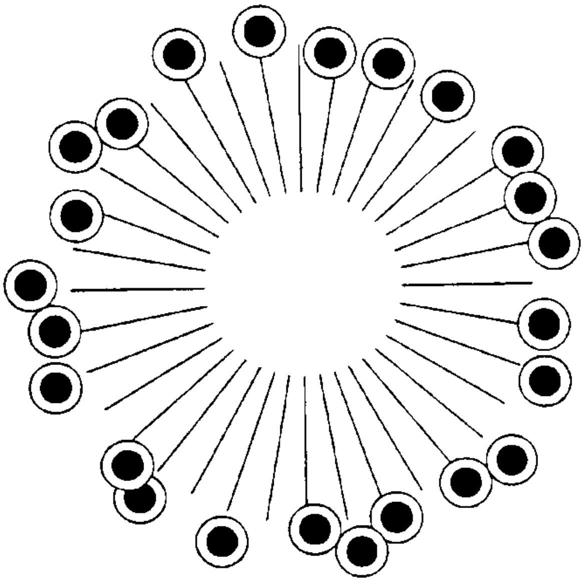


Figure 1.7. An idealized micelle, showing polar, hydrophilic head groups (circles) and hydrophobic chains (lines).

Humic macromolecules may not form true micelles, but because they appear to include distinct hydrophobic and hydrophilic regions (Wershaw, 1986), they might be classified as "self-micelles." As in the case of completely apolar solutes, the formation of micelles is favored by the reduced volume of water cavity space required to surround the micelle relative to its individual molecules, but in addition, the polar regions of amphiphiles are oriented at the surface of the micelle and provide additional solubilizing capacity through ionic interactions, especially if they are charged.

The aggregates of many surface-active compounds are capable of enhancing the solubility of nonpolar organic compounds by bringing them into association with the hydrophobic portion of the amphiphilic cluster (Kile and Chiou, 1989). Humic aggregates and micelles, in particular, may incorporate nonpolar materials such as hydrocarbons, a property that gives them the ability to act as soaps and detergents and transport hydrophobic substances into the aqueous phase (Carter and Suffet, 1982). In the environment, this property becomes important in spills of materials such as petroleum; some of the insoluble hydrocarbons can become incorporated into naturally occurring micelles. For example, dissolved organic matter from seawater was shown to enhance the solubility of *n*-alkanes, but not branched or aromatic hydrocarbons (Boehm and Quinn, 1973). Other investigators, however, have found that the solubility of aromatic hydrocarbons was increased by some samples of humic material (Gauthier et al., 1987); humic substances with higher aromatic carbon content were generally more efficient at binding pyrene. It is possible that dissolved organic matter may enhance solubility of some, especially aromatic, hydrocarbons and quinones by charge-transfer interactions (Kress and Ziechmann, 1977; Melcer et al., 1987). The solubilities of hydrophobic compounds such as chlorinated pesticides have also been reported by many investigators to be enhanced in the presence of humic and fulvic acids (see, e. g., Chiou et al., 1986), although the enhancements vary greatly, depending on the source and chemical characteristics of the humic material (Chiou et al., 1987).

Amphiphilic compounds are also surface-active; their differently polarized regions cause them to accumulate at interfacial zones in the environment. For example, at the air-water interface, amphiphiles tend to orient themselves in "surface microlayers" or "surface films" (see Section 1.B.2d), where the polar region of the molecule is associated with the water phase and the nonpolar region is forced out of solution and extends up into the air phase. Often these surface layers are visible by the damping effect they exert on wave action (Figure 1.8); they are apparent as smoother patches among the ripples on a lake or in the ocean.

6.3. La reazione con cloro

Il cloro, quando disciolto in acqua, si idrolizza secondo la reazione:

$$Cl_2 + H_2O \Rightarrow H^+ + Cl^- + HOCl$$

La costante di equilibrio di questa reazione è 4,5 x 10^{-4} moli L^{-1} a 25 °C e la costante di dissociazione dell'acido ipocloroso HOCl è 2,7 x 10^{-8} moli L^{-1} alla stessa temperatura. Pertanto, la concentrazione di Cl_2 è trascurabile, ed il "cloro libero disponibile" per la disinfezione è costituito dall'acido ipocloroso HClO ed il suo anione ClO^-. Il potenziale standard di elettrodo per la riduzione del cloro a cloruro è di + 1,36 volts. La reazione di ossidazione del materiale organico presente nell'acqua, ivi incluse cellule batteriche, è:

$$HOCl + H^+ + 2\,e^- \Rightarrow HCl + OH^-$$

$$ClO^- + 2\,H_2O + 2\,e^- \rightarrow Cl^- + 2\,OH^- \qquad (5.2)$$

$$HOCl + H^+ + 2\,e^- \rightarrow Cl^- + H_2O \qquad (5.3)$$

are 0.9 V and 1.49 V, respectively (Masschelein, 1979).

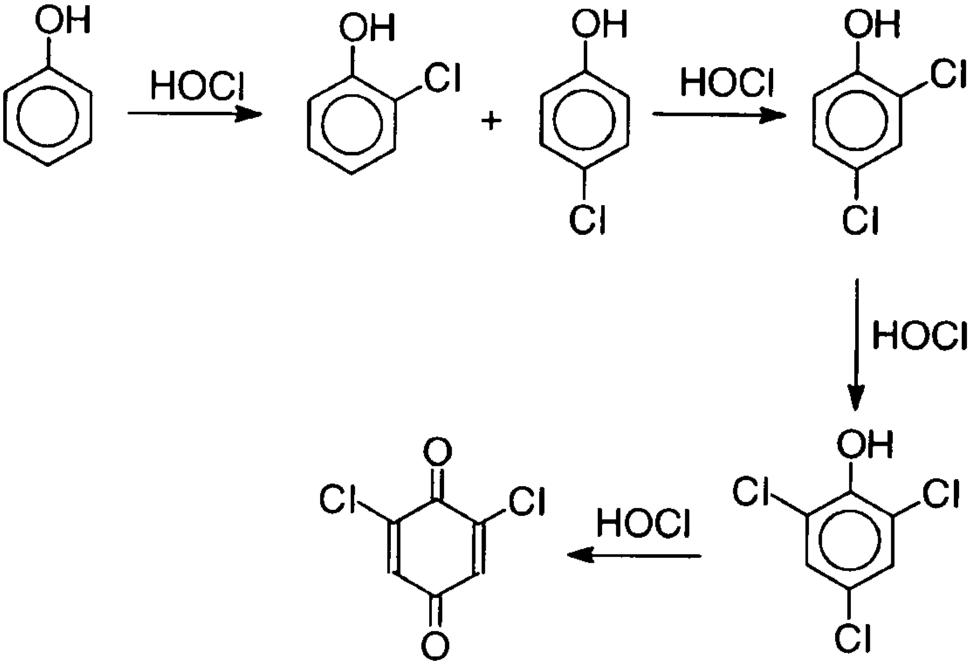
6.3.1. Reazioni con i fenoli

Una delle reazioni più importanti dell'acido ipocloroso è la reattività con i fenoli (che sono importanti perchè contenuti negli acidi umici). Si formano clorofenoli, poichè il fenolo è un composto ricco di elettroni e quindi subisce molto facilmente la sostituzione elettrofila aromatica. Ciò significa che se l'acqua potabile contiene acidi umici, che sono polifenoli, la potabilizzazione con cloro genererà clorofenoli potenzialmente tossici.

La chimica di questa trasformazione avviene attraverso la formazione del reattivo, che è Cl^+, infatti:

$$HOCl \Rightarrow Cl^+ + OH^-$$

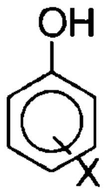
e Cl^+ darà la sostituzione elettrofila sul fenolo.



Si formerà sia l'orto- che il para-clorofenolo, che verranno ulteriormente trasformati in 2,4-diclorofenolo e quindi 2,4,6-triclorofenolo. Questo genererà il 2,6-dicloro-parabenzochinone, prodotto colorato in giallo e responsabile della colorazione che l'acqua contenente fenoli assume quando trattata con ipoclorito.

La natura di sostituzione elettrofila aromatica per questa reazione è dimostrata dalla correlazione tra le acidità di alcuni fenoli e la loro costante di velocità di reazione con HOCl (Figura 6.2).

Le molecole coinvolte in questa correlazione sono nove composti fenolici, il composto non sostituito, i composti aventi un sostituente elettrondonatore, il metile, in posizione orto, meta o para, i composti aventi il sostituente cloro, elettroattrattore per effetto induttivo ma elettrodonatore per effetto mesomero in posizione orto o para, ed i composti aventi il nitrogruppo, sostituente elettronattrattore, in posizione orto, meta o para.



Si nota che tanto meno acido è il fenolo, tanto più alta è la reattività. Questo è spiegabile ammettendo che la reazione consista in un attacco elettrofilo da parte di Cl^+. Infatti, un fenolo sarà poco acido se possiederà un sostituente elettrondonatore che rende difficile la ionizzazione dell'ossidrile fenolico e non stabilizza l'anione fenolato derivante da questa ionizzazione. Questo sostituente aumenterà la densità elettronica sull'anello e renderà più facile la sostituzione elettrofila aromatica.

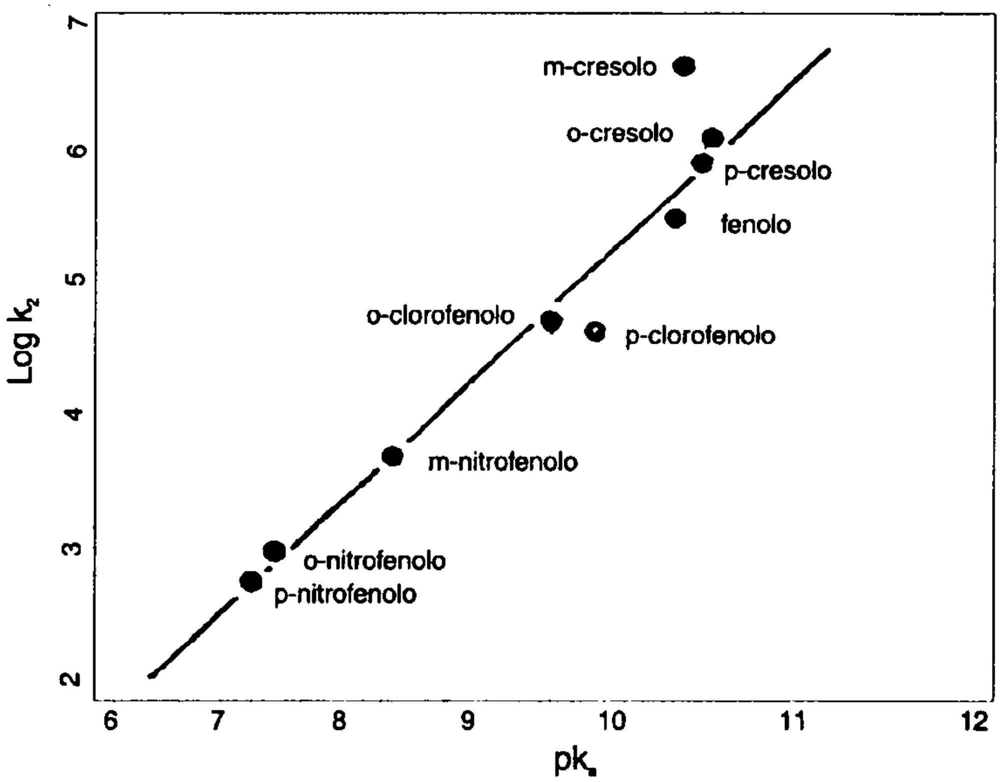
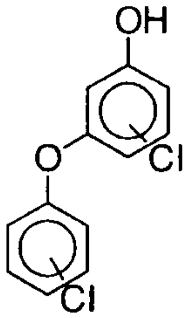


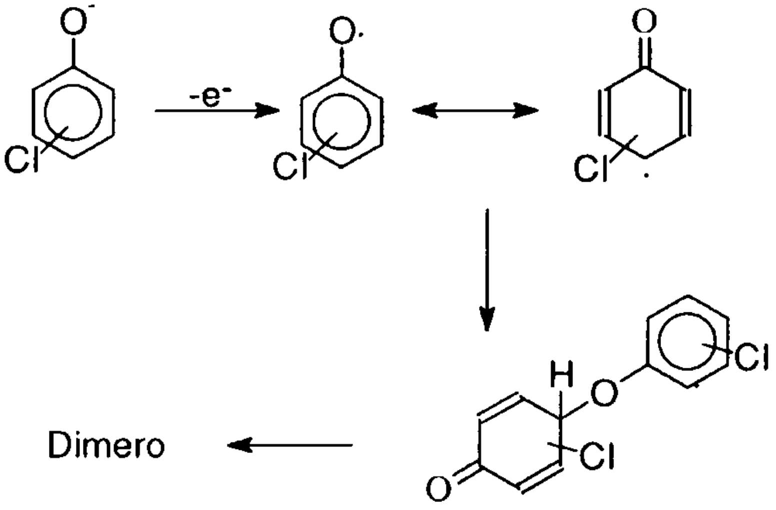
Figura 6.2. Effetto dell'acidità di un fenolo sulla costante di velocità di reazione con HOCl

Naturalmente, questa correlazione non è una correlazione di Hammett, e non sarà quindi possibile valutare l'importanza dell'effetto polare. Tuttavia. L'ordinata in scala logaritmica dice che la differenza di reattività tra il meno ed il più reattivo è di un fattore circa 5.000, niente affatto trascurabile.

Sono stati notati a volte anche composti dimeri. Ad esempio, dal fenolo, difenileteri clorurati:



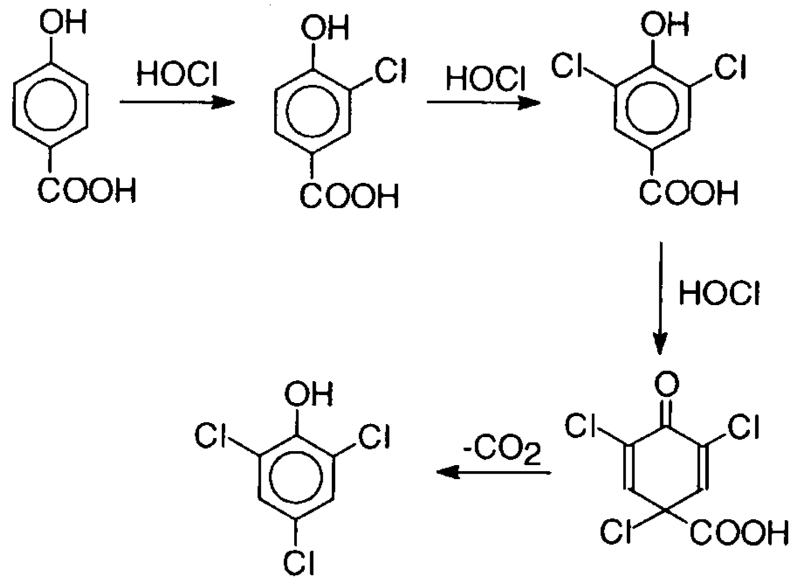
Questi composti fanno pensare ad un meccanismo radicalico, in cui un fenossi radicale formato attraverso un trasferimento di elettrone da un anione fenato possa dimerizzare:

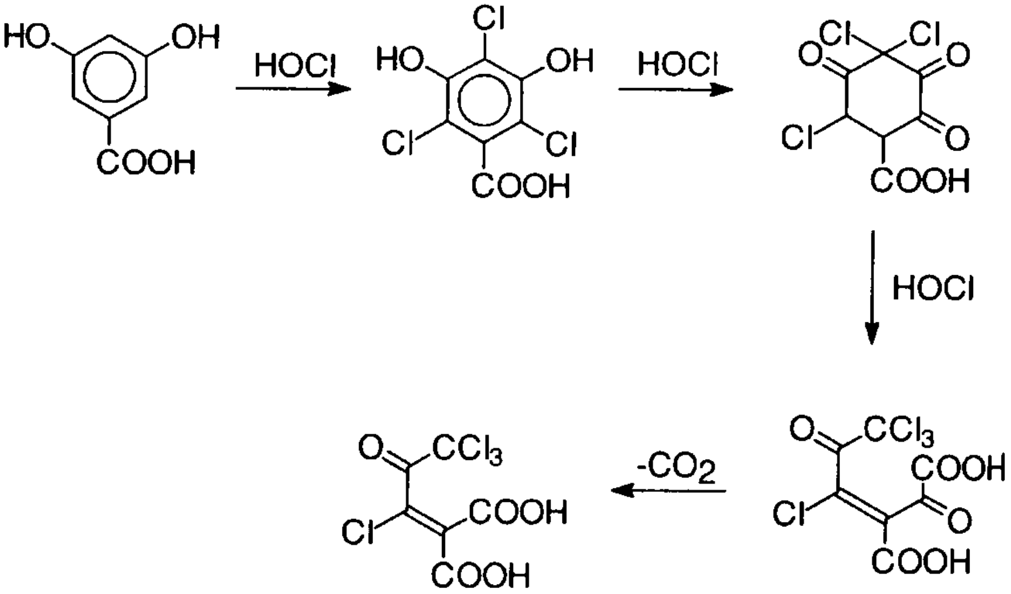


Il reagente capace di effettuare questo trasferimento elettronico potrebbe essere un atomo di cloro, che passerebbe ad anione cloruro.

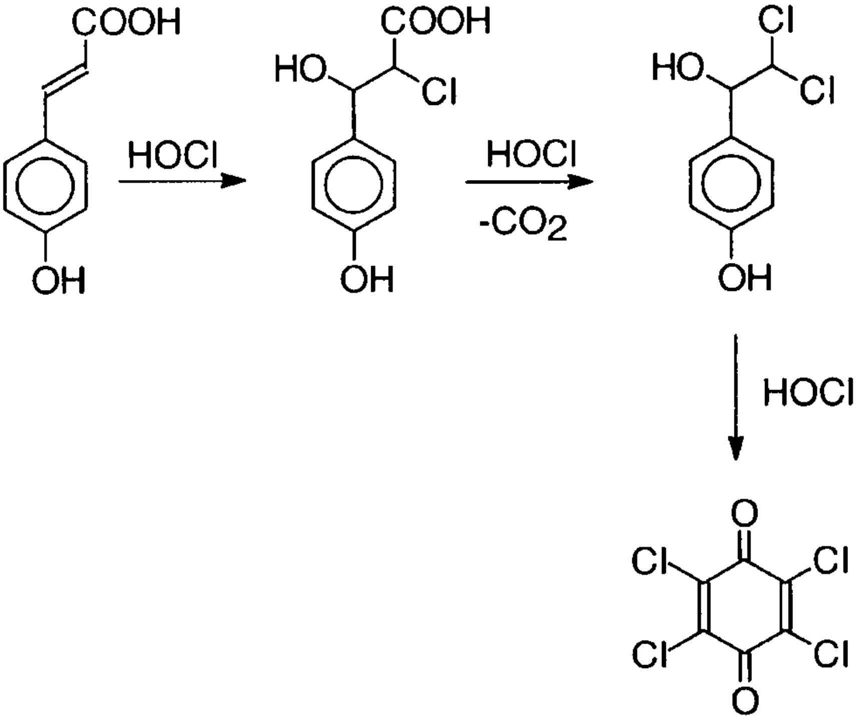
Acidi carbossilici clorurati possono derivare dalla reazione dell'ipoclorito con l'acido 4-idrossibenzoico. In queste condizioni ossidative potrà anche avvenire una decarbossilazione.

Anche l'acido 3,5-diidrossibenzoico, un presunto componente degli acidi umici, subirà l'attacco elettrofilo, che potrà anche giungere alla frammentazione dell'anello aromatico.





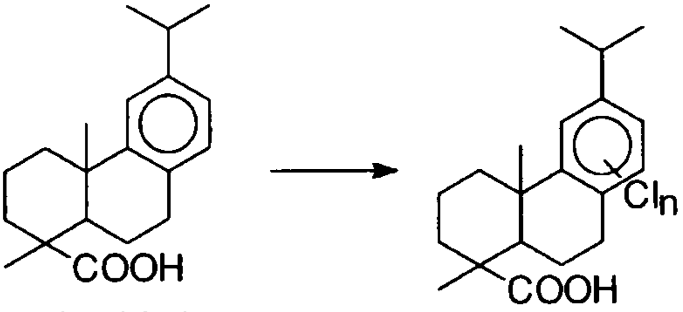
Anche fenili fenilpropenoidici come l'acido 4-idrossicinnamico vengono trasformati in cloroorganici per opera dell'acido ipocloroso.



Qui si ha innanzitutto la formazione di una cloroidrina per attacco di acido ipocloroso al doppio legame. Questo intermedio perde anidride carbonica e, per successiva ossidazione, forma un intermedio che è ulteriormente ossidato fino a tetracloroparabenzochinone.

Come già osservato, molti di questi acidi fenolici sono prodotti di ossidazione di acidi fulvici ed acidi umici. Quindi, è possibile ritenere che un acido fulvico possa essere all'origine di molti composti organici alogenati.

Anche diterpeni aromatici subiscono sostituzione elettrofila aromatica da parte del cloro sul nucleo aromatico.



Acido abietico

Tabella 6.1

I principali prodotti di clorazione di un acido umico

Composti volatili

$CHCl_3$

$CHCl_2-CN$

CCl_3-CHO

Composti non volatili

Acidi monobasici clorurati

$CHCl_2-COOH$

CH_3-CCl_2-COOH

CCl_3-COOH

$CCl_2=CCl-COOH$

Acidi dibasici clorurati

$HOOC-CCl_2-COOH$

$HOOC-CCl_2.CH_2-COOH$

$HOOC-CCl=CH-COOH$

$HOOC-CHCl-CH_2-COOH$

$HOOC-CCl=CCl-COOH$

Acidi tribasici clorurati

$CCl_3-CO-CCl=C=(COOH)_2$

Intermedi del cloroformio

$CCl_3-CHOH-CCl_2-CHCl-COOH$

Acidi cicloalcanoici

$NC-CH_2-CH_2-CH_2-COOH$

$NC-CH_2-CH_2-COOH$

Acidi alcanoici

$CH_3-(CH_2)_n-COOH$

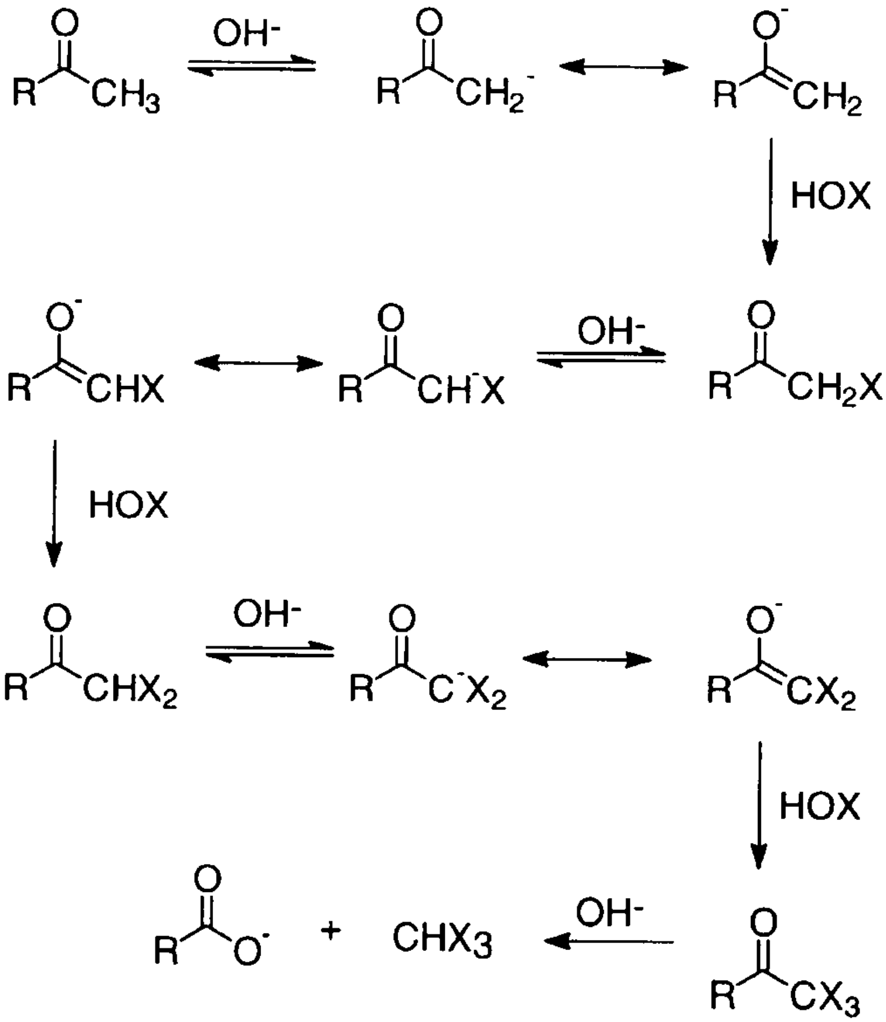
Acidi alcandioici

$HOOC-(CH_2)_n-COOH$

Acidi benzencarbossilici

$C_6H_5-(COOH)n$

La reazione dell'aloformio consiste nella trasformazione di un metilchetone in un acido carbossilico più un aloformio. Si ha progressiva alogenazione del metile del metilchetone. Quando si arriva alla completa alogenazione del metile, la molecola si spezza perchè il carbonio carbonilico è diventato molto elettrofilo e reagisce rapidamente con OH^-. Si otterranno i prodotti di reazione che saranno generalmente un acido carbossilico ed un aloformio.



L'importanza di questo fenomeno risiede nel fatto che nella struttura degli acidi umici, oltre a gruppo carbossilici e gruppi fenolici, vi sono gruppi metilici attribuibili alla struttura di metilchetoni.

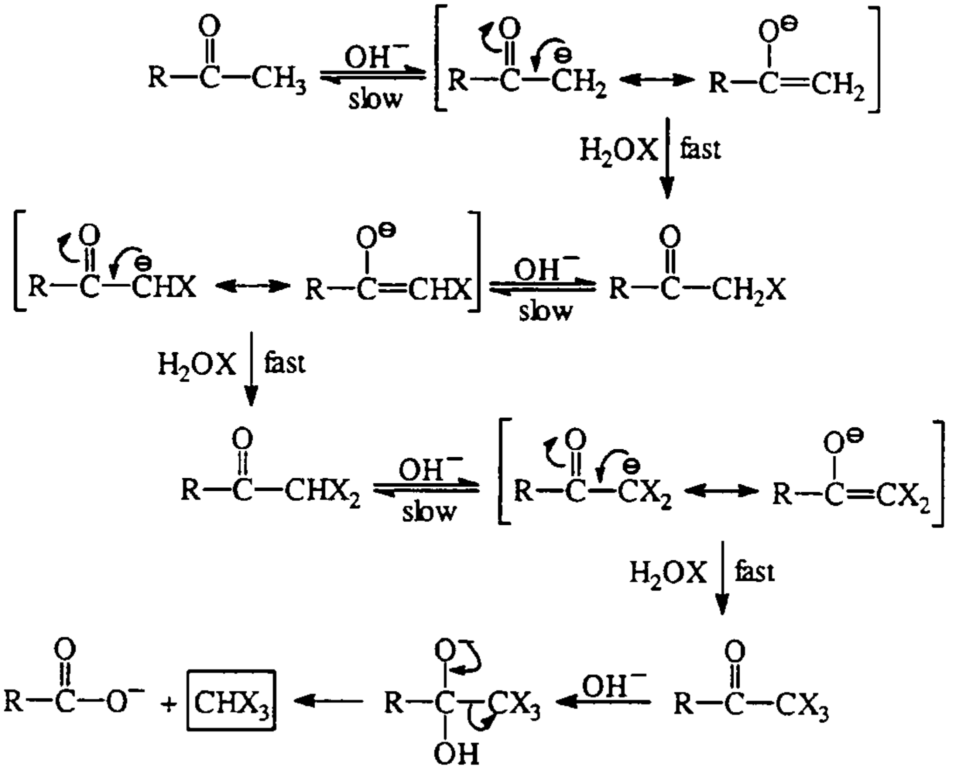


Figure 5.5. Mechanism of the haloform reaction with methyl ketones. From Morris and Baum (1978). Reprinted by permission of Lewis Publishers.

6.3.2. Reazioni con le ammine

In presenza di ione ammonio in soluzione, l'acido ipocloroso forma cloroammine:

$$NH_4^+ + HOCl \Rightarrow NH_2Cl + H_2O + H^+$$

$$NH_2Cl + HOCl \Rightarrow NHCl_2 + H_2O$$

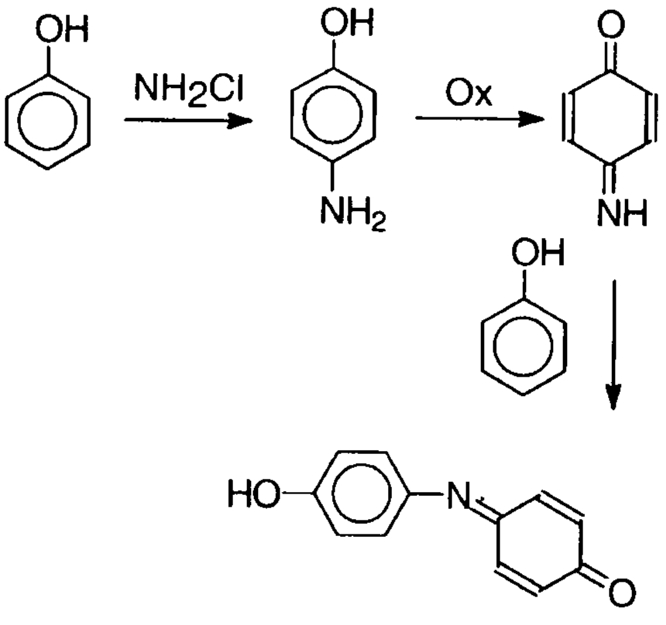
$$NHCl_2 + HOCl \Rightarrow NCl_3 + H_2O$$

Le tre cloroammine si dicono "cloro combinato disponibile". Questa procedura viene spesso utilizzata quando si voglia eliminare l'ammoniaca da un'acqua potabile. Infatti, per quantità moderate di azoto ammoniacale, la cloroammina inizialmente formata reagisce ulteriormente con l'acido ipocloroso:

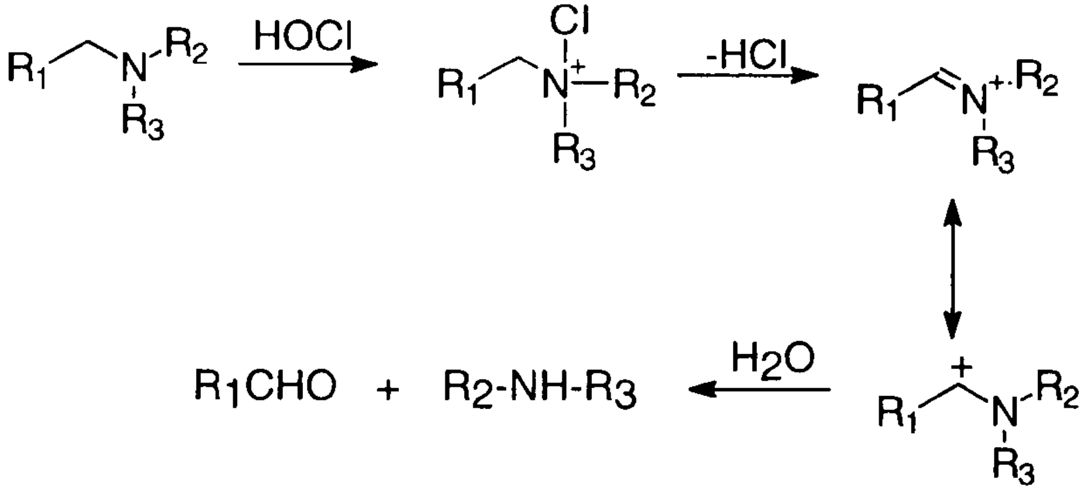
$$2\ NH_2Cl + HOCl \Rightarrow N_2(g) + 3\ HCl + H_2O$$

dando luogo a denitrificazione. Se la quantità di cloro è sufficientemente elevata rispetto a quella dell'ammoniaca si ha il "breakpoint". La disinfezione deve avvenire sempre con rapporti Cl/NH_4^+ più elevati del breakpoint.

La reazione di NH_2Cl con il fenolo forma il blu di indofenolo.



La figura 6.4 mostra la reattività della ammine nei riguardi dell'acido ipocloroso. Essa è più alta quanto più alta è la basicità dell'ammina. La ragione di ciò è la quaternizzazione dell'azoto ad opera del Cl^+, con conseguente formazione di uno ione immonio e successiva rottura idrolitica. La reazione di HClO (o meglio di Cl^+) in presenza di ammina è in pratica una N-dealchilazione ossidativa, ossia porta all'ottenimento di un'ammina con una catena alchilica in meno e di un aldeide.



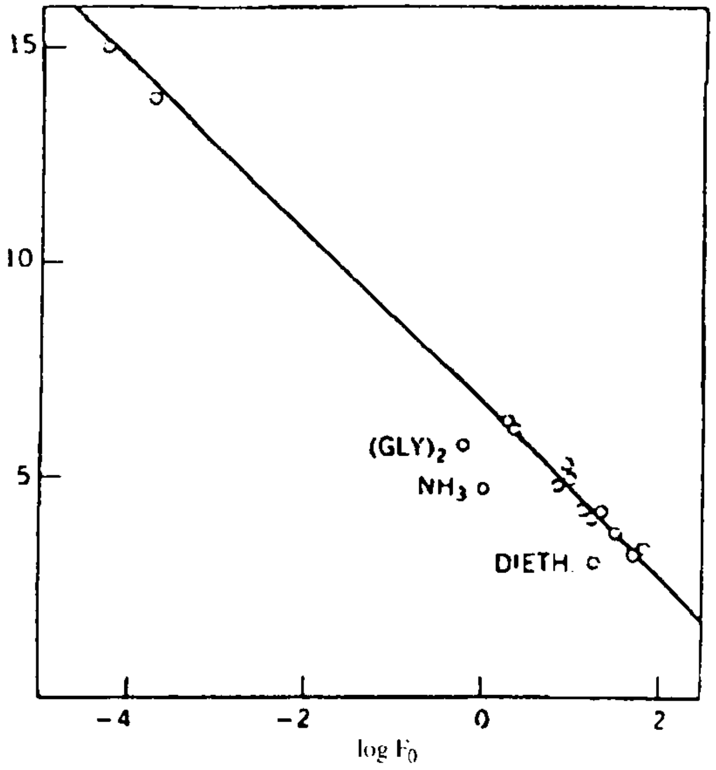
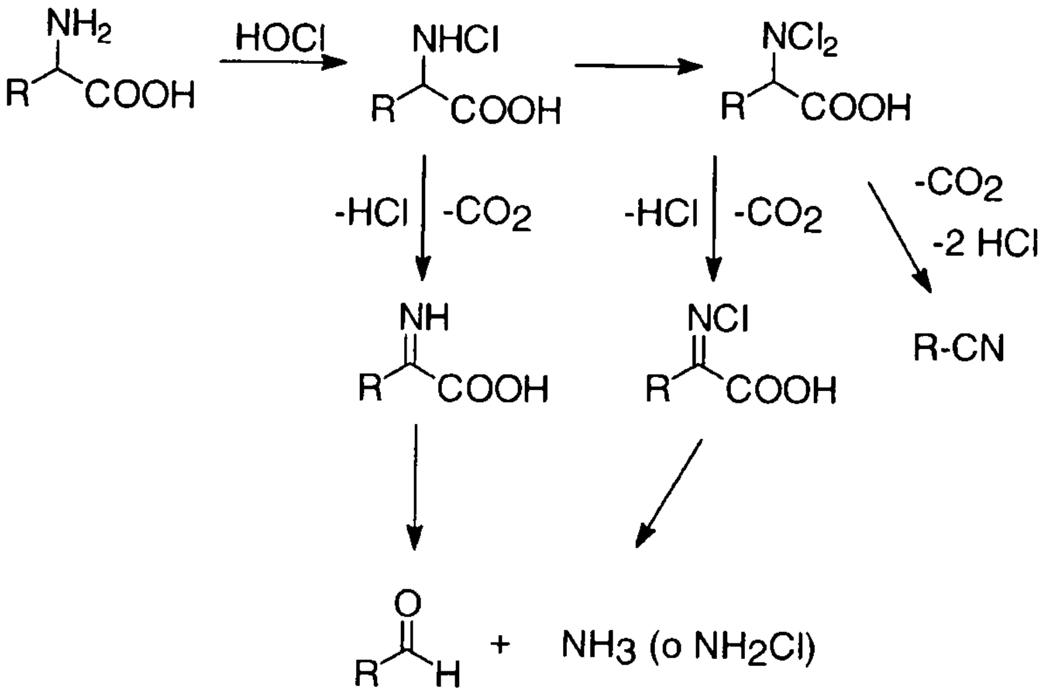


Figura 6.4. Correlazione tra la basicità delle ammine e la velocità di reazione con HOCl

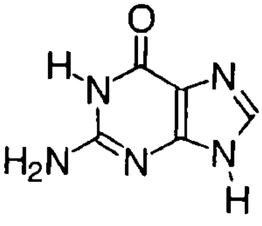
6.3.3. Reazione con gli amminoacidi

Anche nel caso degli amminoacidi si forma inizialmente una N-alogeno ammina, seguita da decarbossilazione e si forma un'aldeide. Se si forma inizialmente la N,N-dialogenoammina si avrà alla fine anche un nitrile.

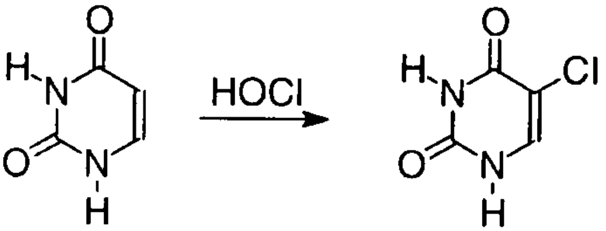


6.3.4. Reazione con gli eteroaromatici

Le basi puriniche, come la guanina, sono molto poco reattive all'acido ipocloroso. Le basi pirimidiniche sono invece reattive. Ad esempio, l'uracile viene inizialmente trasformato in 5-clorouracile, e successivamente demolito.



Guanina



Uracile

6.4. Reazioni con il biossido di cloro

La formazione di cloroformio per clorazione di acque contenenti acidi umici è stata dimostrata sperimentalmente. Per questa ragione, la clorazione è stata sostituita dal trattamento con il biossido di cloro, ClO_2, che non produce cloroformio. Esso ossida a pH neutro secondo l'equazione:

$$ClO_2 + 5\,e^- + 4\,H^+ \Rightarrow Cl^- + 2\,H_2O$$

Il potenziale standard di elettrodo è di + 1,50 volts, simile a quello della coppia MnO_4^-/Mn^{2+}. ClO_2 è gassoso ed esplosivo. Pertanto viene generalmente prodotto "in situ" attraverso la reazione:

$$Cl_2(g) + 2\,NaClO_2(s) \Rightarrow ClO_2(g) + 2\,NaCl(s)$$

Tipicamente, si miscela una soluzione di sodio clorito al 26% con una soluzione di acqua di cloro contenente 0,5-1 g L^{-1} di cloro. Il biossido di cloro ha attività battericida e viricida molto elevata.

ClO_2 è difeso dai produttori di cloro; è un reagente a basso costo (minore dell'ozono), è un prodotto dell'industria del cloro che così può sopravvivere; è, assieme all'ozono, un'alternativa al cloro.

ClO_2 è un radicale e reagisce con gli alcani RH per dare $HClO_2$ ed un radicale al carbonio R· che poi alimenterà una reazione di autoossidazione.

$$ClO_2 + RH \Rightarrow R\cdot + HClO_2 \qquad \text{Acido cloroso}$$

$$R\cdot + O_2 \Rightarrow RO_2\cdot \Rightarrow \text{prodotti}$$

$HClO_2$ in generale dismuta ad $HClO$ e $HClO_3$ e questo è un problema perchè significa che questo sistema genera acido ipocloroso, e quindi Cl^+. Si avrà quindi la reazione di sostituzione elettrofila aromatica e quindi in questo senso ClO_2 non risolve il problema di non generare cloroorganici. In generale, la produzione di Cl^+ si ha in pratica (più o meno difficilmente) con tutti gli $HClO_x$.

Acido ipocloroso

$$2\,HClO_2 \Rightarrow HClO + HClO_3 \qquad \text{Acido clorico}$$

Infatti, nella reazione dello stilbene con ClO_2 si ha attacco ai due nuclei benzenici con formazione dell'epossido e di un prodotto cloroorganico. L'introduzione del cloro al nucleo aromatico è probabilmente dovuta alla presenza di Cl^+.

Humic materials. The so-called "humic substances" are probably the most abundant polymers in nature. The standing crop of humic materials in the soil has been estimated to be approximately 2–3 × 10^{12} tons (Bazilevitch, 1974). They are brown, acidic materials which bear no immediately apparent resemblance to conceivable precursor materials, and appear to be formed by oxidation and condensation reactions between polyphenols, polysaccharides, and polyamino acids of plant and microbial origin. As Hurst and Burges (1967) pointed out, "This situation is undoubtedly the most complicated and variable existing in nature." Despite nearly two centuries of investigation, environmental chemists still cannot agree on a rational structure for humic substances or on mechanisms for their formation.

Humic materials of soil are intimately bound to its mineral constituents. They are polyelectrolytes, bearing strong negative charges, and are associated with metallic cations such as those found in clays. No single organic solvent is useful for the extraction of more than a small fraction of soil carbon. Water is likewise a poor extractant, although some polymeric material having osmometrically determined mean molecular weights of a few hundreds can be removed. The most commonly used efficient extractant is aqueous alkali; typically soil is shaken under N_2 with 0.5% NaOH, the suspension is centrifuged, and the aqueous layer is decanted. In the traditional workup of soil organic matter extracts, the alkaline fraction is next acidified, usually causing the precipitation of a large fraction of the soluble material. This base-soluble, acid-insoluble humic fraction is called *humic acid*. Organic material remaining in solution after acidification is referred to as *fulvic acid*. (Whether the two fractions differ sufficiently in their chemistry to warrant separate classifying names is doubtful.) Further distinctions are sometimes made; for example, organic carbon which cannot be extracted from soil by alkali has been called *humin*.

No universally accepted technique has materialized that permits a reproducible subfractionation of humic and fulvic acids. Humic acid polymers can often be largely freed of small molecular contaminants, both salts and organic impurities, by dialysis. Fulvic acids, however, appear to consist of smaller molecules or aggregates, and attempts to dialyze them result in large losses of organic carbon to the medium. Adsorption, partition, and ion-exchange chromatography techniques have been employed to some extent. In general, ion-exchange techniques have not been widely used because of the problem of contamination by impurities from the resin, and because it is quite difficult to achieve complete desorption of the humic material from the resin.

Similar difficulties have plagued attempts to fractionate humic materials by adsorption chromatography. Charcoal, alumina, and other adsorbents have been tried with limited success. The most widely used method of fractionation for soil humic materials has been gel permeation chromatography. Although some work has been done using controlled-pore glass and polyacrylamide beads, most investigators have used Sephadex® dextran gels. These materials are available with a wide range of molecular exclusion properties (different degrees of cross-linking) based on pore size; ideally, molecules whose dimensions are smaller than the pore sizes of the gel are held up within the pores and elute from the column later than large molecules which are excluded from the pores. In practice, the method works well for relatively homogeneous mixtures such as closely related proteins or polysaccharides, but mixtures of polydisperse, chemically different substances such as humic materials also exhibit different electrostatic interactions with the dextran gel material. In particular, polyphenolic materials display strong hydrogen bonding and are eluted much later than would otherwise be predicted (Brook and Munday, 1970). Thus, a significant fraction of a humic mixture is likely to display an apparent molecular size much smaller than the "true" value. Fractionation of humic materials by dextran gel filtration may be useful for comparative purposes, but probably not for the assignment of molecular weight distribution without careful consideration of other variables. Many other methods of molecular weight determination have been applied to soil humic preparations, but none has been entirely successful (Wershaw and Aiken, 1985).

Ultimate analyses of many soil humic substances have been reported. The dominant elements are carbon (40–65%) and oxygen (30–50%); a selection of values is given in Table 1.11. In general, humic acids are somewhat higher in carbon and lower in oxygen than fulvic acids. Nitrogen content almost always ranges from 1% to 6%, hydrogen from 3% to 6%. Few determinations of other elements have been

Table 1.11. Mean Elemental Composition of Selected Humic Materials (in %)

	C	H	N	O	S
Soil humic acid	57.3	5.0	2.8	34.4	0.6
Coal humic acid	64.8	4.1	1.2	28.7	1.2
Soil fulvic acid	47.0	4.4	1.5	46.4	0.7
Water fulvic acid	46.2	5.9	2.6	45.3	—

Source: Schnitzer and Khan (1972).

performed; sulfur and phosphorus appear usually to be present to the extent of a few tenths of a percent, at most.

Stevenson and Butler wrote (1969), "A variety of functional groups, including COOH, phenolic OH, enolic OH, quinone, hydroxyquinone, lactone, ether and alcoholic OH, have all been reported in humic substances, but there is considerable disagreement as to the amounts present; in some cases even proof of existence is lacking." Matters have not improved significantly in the intervening couple of decades. There is a paucity of analytical methods which are sufficiently precise and free from interferences for reliable determination of organic functionalities in complex polymers such as humic materials. Published infrared and ultraviolet spectra of humic substances are generally of little or no value for this purpose because of their lack of resolution or fine structure, as would be expected for complex mixtures.

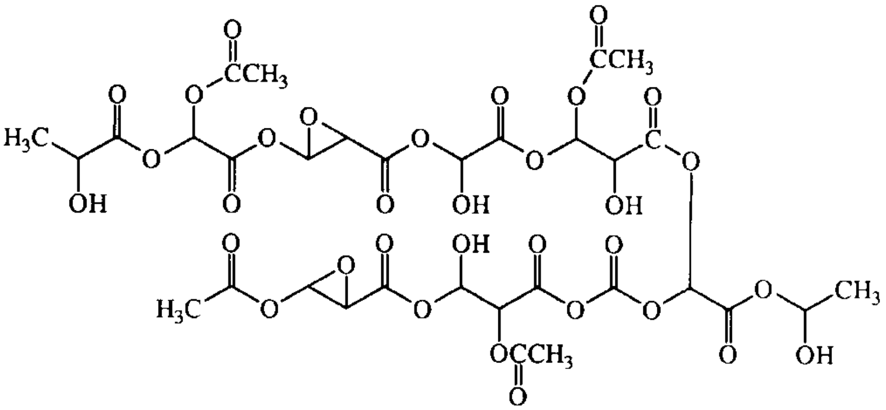
Probably ^{13}C and ^{1}H NMR spectroscopy have provided the most useful information about the general characteristics of the structures of humic substances. After a brief summary of the findings from these spectra, we will turn our attention to other methods, such as functional group analyses and chemical degradation studies, and finally give a selection of type structures that have been proposed by various researchers over the past 30 years.

in the ^{13}C-NMR spectra of soil humic and fulvic acids.

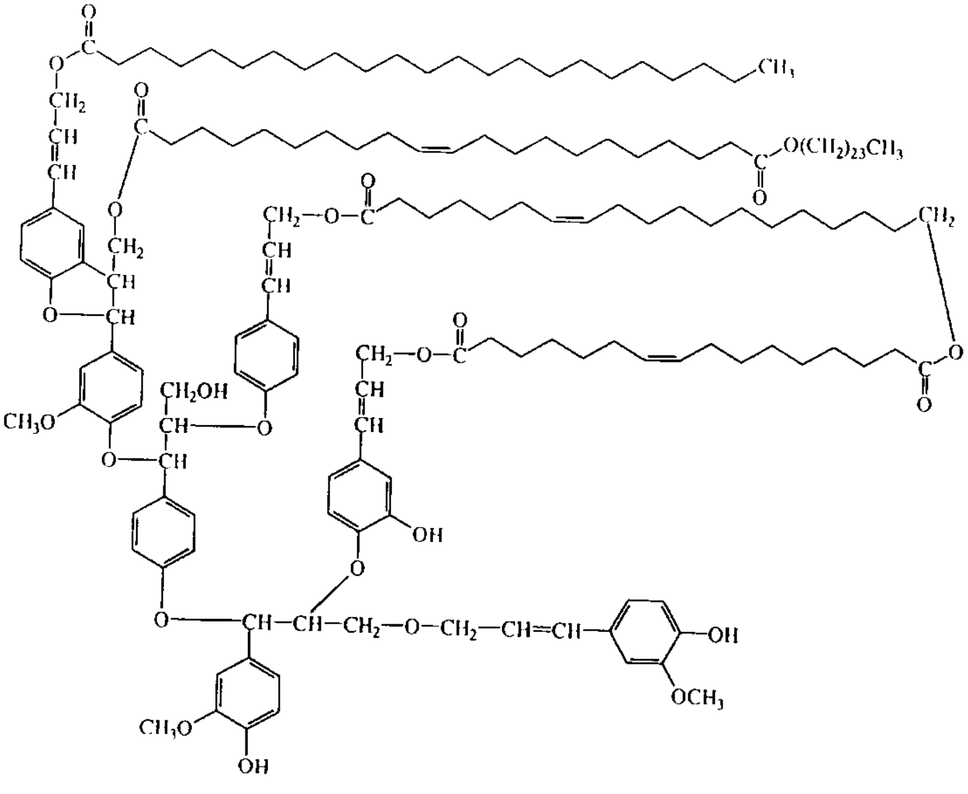
An interesting hypothesis for the origin of aliphatic structures in humic materials has been put forth by Tegelaar et al. (1989). These authors have suggested that

---

polymers such as cutin (**36**) and suberin (**37**), polyester derivatives that play an important role in protecting external and internal organs of many higher plants, as



36



37

well as other poorly characterized aliphatic biopolymers, might be important precursors because of their abundance and resistance to degradation. They also called attention to the occurrence of poorly characterized, highly aliphatic substances characteristic of the cell walls of some algae. Goni and Hedges (1990) demonstrated that copper oxide oxidation products of cutin, long-chain hydroxy fatty acids, were similar to those observed when sediment-derived humic substances were oxidized by the same reagent.

The distribution of OH groups in humic materials has been examined by Mikita et

Table 1.15. Distribution of Oxygen Functional Groups in Humic Materials

Group	meq/g	% of Total O (range)
–COOH	5.1	13.6–65.0
Phenolic –OH	3.6	9.1–38.0
Aliphatic –OH	3.0	0.9–16.4
C=O	3.2	4.1–28.7
–OCH$_3$	0.5	1.0–9.4

Source: Mean of 7–11 determinations reported by Schnitzer and Khan (1972).

Models for the structure of humic materials. Leenheer et al. (1989) have pointed out that the notion of a "general," "average," or "type" structure for humic substances is controversial, with some investigators believing that such mixtures are so innately diverse and heterogeneous that structural models have little meaning. On the other hand, other workers believe that attempts to synthesize the available information into approximate or figurative representations are of value in helping to predict the physical, biological, and chemical consequences of the presence of humic materials in the environment. In any event, a few investigators have attempted to synthesize the information available about humic substances into general or type structures. These structures display a wide range of chemical complexity and sensitivity to mechanistic concepts. They tend to fall into two general categories: first, "uniformist" models that try to explain all of the properties of humic compounds in terms of a very simple series of reactions or structures; and secondly, "eclectic" models characterized by the incorporation of all kinds of subunits of very diverse chemical nature. We present in this section a very limited selection of the wide variety of proposed structures available in the literature to give some insight into the thought processes that have gone into the models.

A very early model by Fuchs (Figure 1.22; see Swain, 1963) featured a highly condensed aliphatic and aromatic ring system substituted by carboxyl and phenolic hydroxyl groups. The structure appears to have been influenced by the flat, polychair hexagonal structure of graphite and also by early models for coal which depicted it as largely made up of planar polyaromatic hydrocarbons. It is not entirely clear how such a structure could arise from naturally occurring precursors. This model was influential for a time because it illustrated a central "core" region with highly conjugated double bonds, which would account for the color of humic materials, and allowed for flexible modes of attachment of chains of other functionalities, which could be chosen more or less randomly according to which properties of the humic structure the proposer wished to emphasize.

Another type of uniformist model is that of Flaig (1950, Figure 1.23) which considered humic materials to be polyphenol ethers. This sort of structure appears

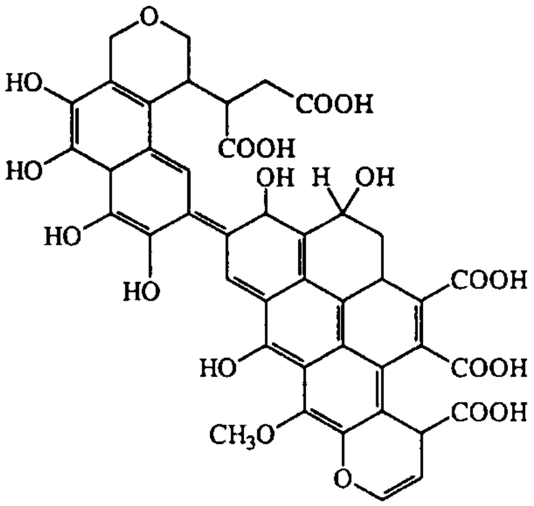


Figure 1.22. Fuchs' model for humic acid structure. From Swain (1963). Reprinted by permission of Pergamon Press.

to be inspired by the indisputable fact that solutions of polyphenols such as pyrogallol and hydroquinone turn brown on standing, especially in the presence of alkali.

The apparent source materials for forming such a hypothetical humic polymer would be lignin degradation products or plant polyphenols such as flavonoids. Because it has little relationship with the physical or chemical characteristics of actual humic materials, this type of model has fallen out of favor almost completely, except for ambiguous statements, still occasionally encountered, that the color of natural waters is due to "tannins."

Schnitzer and Khan (1972) proposed a structure for fulvic acid that pictures it as an assemblage of small aromatic molecules, held together by hydrogen bonds (Figure 1.24). The model is derived from results of oxidative degradation studies of humic materials in which the largest group of identifiable products was a number of aromatic polycarboxylic (3 to 6 -COOHs per benzene ring) acids (see, e.g., Schnitzer and Ortiz de Serra, 1973). Although this formulation looks simplistic by today's

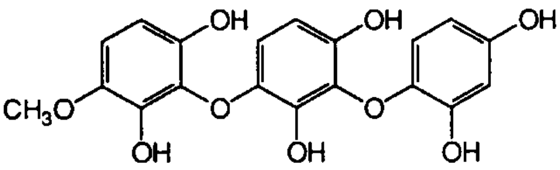


Figure 1.23. Flaig's model for humic acid structure. From Swain (1963). Reprinted by permission of Pergamon Press.

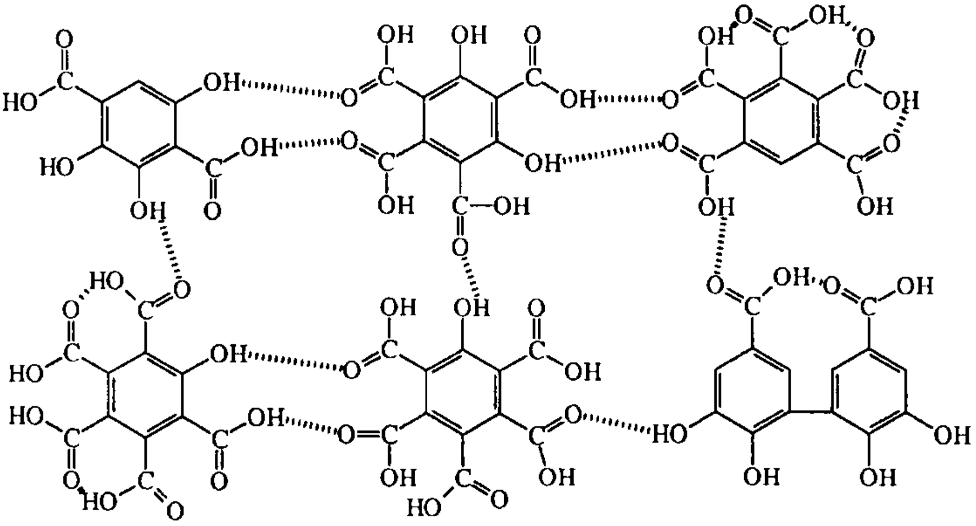
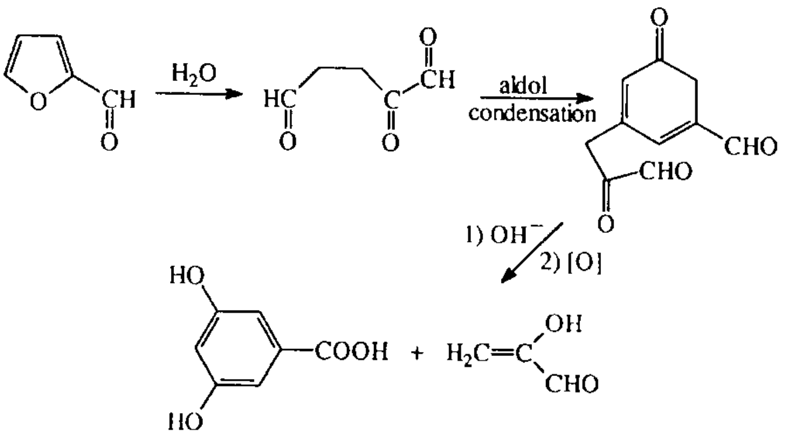


Figure 1.24. Schnitzer and Kahn's (1972) model for fulvic acid structure. Reprinted by permission of Marcel Dekker, Inc.

standards, it is difficult to better reconcile the observed degradation products from humic materials with rational precursors for them that might be incorporated in a larger type structure. It has, however, been demonstrated that benzenecarboxylic acids are formed even when apparent structurally unrelated polymers, such as polysaccharides, are subjected to oxidizing conditions (Cheshire et al., 1968; Almendros and Leal, 1990). The mechanisms of formation of aromatic compounds from carbohydrate precursors are uncertain, although simple sugars have been reported to yield



(1.51)

aromatic products when heated under mildly acidic conditions (Popoff and Theander, 1972, 1976). Cheshire et al. (1968) proposed that aldol condensations between two molecules of a five-carbon keto aldehyde derived from furfural hydrolysis (Reaction 1.51) could give rise to phenolic acids.

A uniformist structure for marine humic substances (Figure 1.25) was proposed by Harvey et al. (1983). This model takes as its starting point the polyunsaturated lipids of marine planktonic organisms. As the figure shows, a polyunsaturated triglyceride can be hypothetically converted via free-radical reactions to form interstrand linkages that might become partially aromatized by oxidation and dehydra-

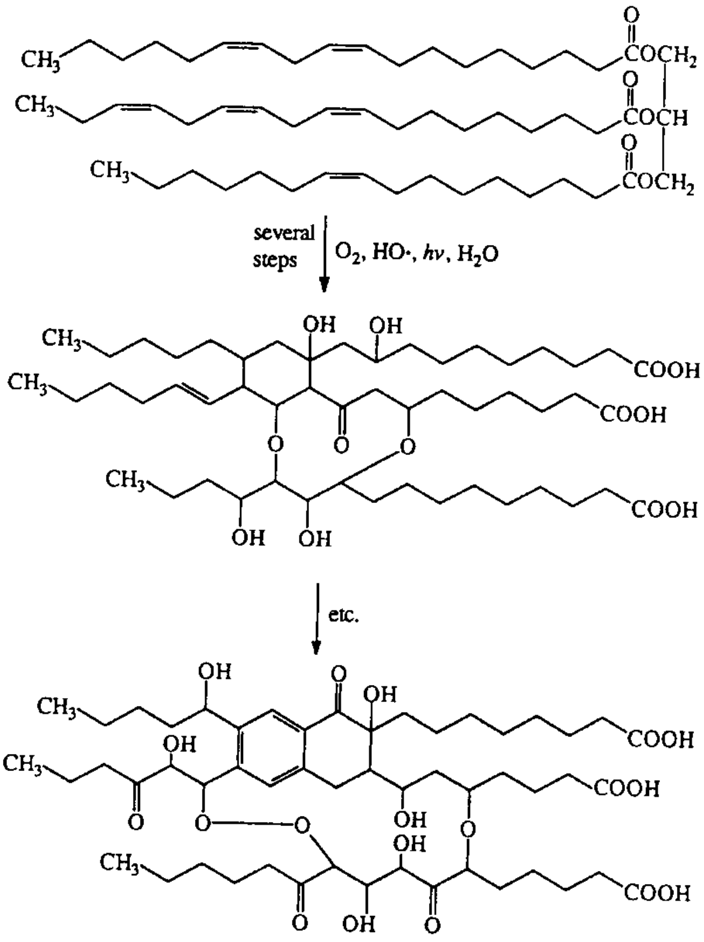


Figure 1.25. Harvey and Stanhauer's model for the structure of marine humic substances. From Harvey and Stanhauer (1983). Reprinted by permission of Elsevier Scientific Publishers.

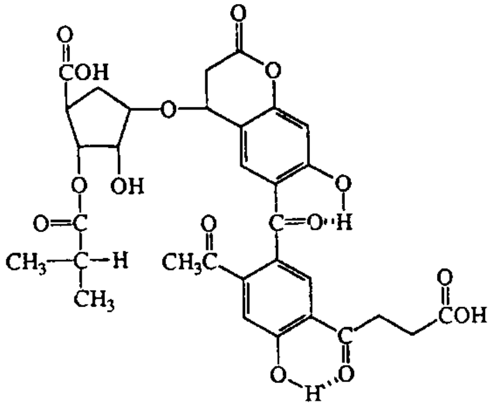


Figure 1.26. Leenheer's "average structural model" for freshwater fulvic acid. Reprinted from R. C. Averett et al., "Humic Substances in the Suwanee River, Georgia: Interactions, Properties, and Proposed Structures," U.S. Geological Survey report #87–557,

tion. After ester hydrolysis, the type structure is revealed as a largely aliphatically substituted aromatic (1-tetralone) structure containing carboxyl, carbonyl, alcohol, and peroxide groups. The structure proposed is intriguing and ought to lend itself to testing through model compound reactions.

Perhaps the ultimate uniformist model was proposed by Anderson and Russell (1976), who stated that fulvic acid had many of the properties of a synthetic polymer, polymaleic acid. This polymer could be represented as $[\text{-CHCOOH-}]_n$, by analogy with polyethylene, although other structures such as anhydrides, cyclopentanone units, and keto olefinic structures have been suggested to be present. The polymer was shown to differ in many important respects such as its UV, fluorescence, and ^{13}C NMR characteristics from an authentic fulvic acid (Spiteller and Schnitzer, 1983).

Leenheer et al. (1989) proposed several semieclectic "average structural models" for a fulvic acid isolated from a highly colored river water. The parameters chosen for the models were designed to agree with the extensive spectroscopic and chemical data available for this material, and were also based on hypothetical reactions that could have transformed known plant-derived compounds into the fulvic acid. The average molecular formula for the models was taken to be $C_{33}H_{32}O_{19}$, based on molecular weight and elemental composition analyses. Nitrogen, sulfur, and phosphorus were not incorporated into the model structures due to their low abundance in the fulvic acid. One of these structures is shown in Figure 1.26.

One example of extreme eclecticism in a humic model is Gjessing's (1976; Figure 1.27); there are many other examples like this, mostly sharing the same apparent reluctance to discriminate among all possible environmental reactants.

To conclude, it is apparent that despite more than a century of work on humic

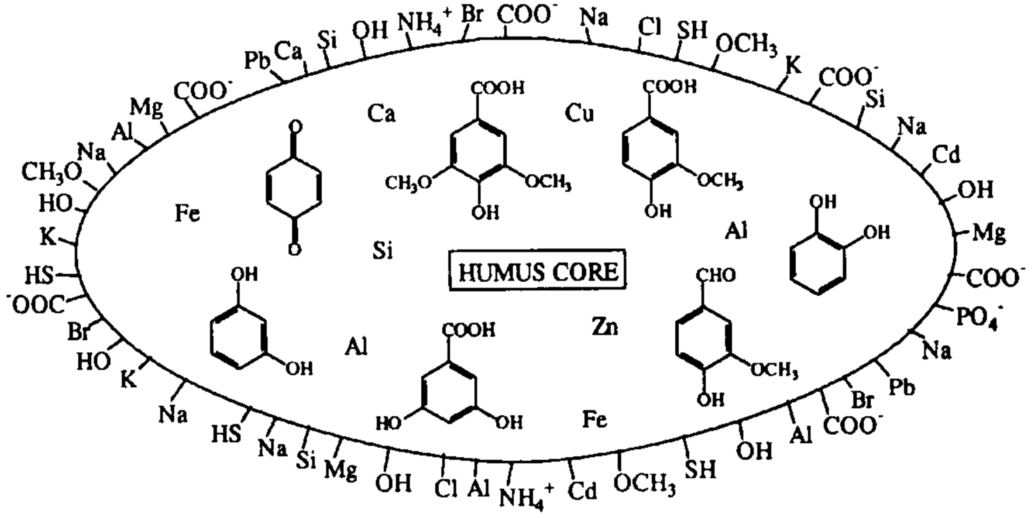


Figure 1.27. Gjessing's (1976) "eclectic" concept of humic material. Reprinted by permission of Lewis Publishers.

materials, we still have only a very approximate and incomplete understanding of their molecular characteristics. It is to be hoped that in future years we will have a much better conception of the chemical nature of these important polymers.