

Molecular Iodine Reduction by Natural and Model Organic Substances in Seawater

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(Received: 2 August 1994; accepted: 16 December 1994)

Abstract. The reactivity of 2 μM molecular iodine in seawater toward various organic compounds containing aromatic, α -keto, amino, olefinic and sugar functional groups was investigated. More detailed studies have been made of the reduction kinetics with salicylic acid, α -ketoglutaric acid and the polypeptide oxidized glutathione, particularly to establish whether variation over the pH range 4–9 would provide a similar reduction reactivity or “fingerprint” to that of molecular iodine added to natural seawater. The data indicates that compounds with only one functional group react with first order kinetics whereas compounds with multiple functional groups show more complex behaviour. Kinetic and thermodynamic modelling indicates that HOI is the main iodine species reacting with organic matter at seawater pH of 8.2. Based on the pH “fingerprints”, peptides and compounds containing carbonyl or α -keto groups are the key reductants of molecular iodine added to seawater. These compounds form C–I and N–I bonds which can allow for a rich organic iodine chemistry in seawater. The model compound results are discussed in relation to oceanic processes.

Key words: Molecular iodine, iodination kinetics, iodine speciation, organic iodine.

1. Introduction

Truesdale (1974) found that micromolar amounts of molecular iodine added to seawater are reduced within hours, and hypothesised that organic material was responsible. To avoid any possible confusion, here the molecular iodine species, I_2 , will be written as such, and the saturated iodine solution used for inoculating seawater, as M.I. He demonstrated that the reaction displays a rapid initial phase followed by a much slower one, and is saturated by the addition of about 10^{-4} M of M.I. The reaction appears to have counterparts in the addition of chlorine and ozone to seawater during anti-fouling measures with power station cooling waters (Eppley *et al.*, 1976; Richardson *et al.*, 1981; Wong and Oatts, 1984). It has been suggested (Miyake and Tsunogai, 1963) that I_2 could be generated at various marine interfaces, e.g., the sea surface through the action of UV light on iodide, and through the reduction of iodate. If this is so, the reduction reaction for M.I. would provide serious competition to the disproportionation reaction which results in IO_3^- formation, and it is interesting to speculate as to what the relative rates would have to be to enable one reaction to swamp the other.

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As part of a trend toward quantifying such rate-determined systems the kinetics of the reduction process have been modelled, firstly, as a series of first order reactions involving two different iodine species (Truesdale and Moore, 1992; Truesdale, 1993), but later, as the oxidation by M.I. of two types of organic material, one of which is rapidly consumed (Truesdale *et al.*, 1995). The establishment of the second of these rate equations enabled Truesdale *et al.* (in press) to demonstrate the environmental insignificance of the disproportionation reaction of molecular iodine species to iodate in surface seawater in which molecular iodine was earlier thought to be capable of forming iodate in seawater (Sugawara and Terada, 1958).

Remembering how the "iodine number" has been used classically to characterise unsaturated compounds we believe that the reduction reaction may ultimately be useful hydrographically as a means of differentiating between seawaters, and chemically as a means of characterising their organic components. Accordingly, here we have been interested to study the reaction further to try and ascertain which types of model organic compounds would react with molecular iodine in a similar manner as the natural organic compounds in seawater. Initially this only demands the screening of compounds, or at least functional groups, which will reduce micro-amounts of iodine in seawater. Subsequently however, there is a need to design means by which the more environmentally likely compounds may be identified. In this paper we present the results of some screening tests while also showing how the variation of a compound's reduction rate with pH, its "pH-fingerprint", can be used in overcoming the second problem. The organic compounds chosen reflect the types of functional groups expected in estuarine, nearshore and offshore waters (Lee and Wakeham, 1988).

Finally, the reaction of M.I. with seawater and with model organic compounds provides insight to the incorporation of iodine into organic matter and the cycling of iodine in the ocean. Dissolved organic iodine has been observed in productive areas (Luther and Campbell, 1991; Luther *et al.*, 1991; Ullman *et al.*, 1991) as the difference between total iodine and the sum of iodide plus iodate. Particulate organic iodine is transported from the surface ocean to the ocean sediments (Deuser *et al.*, 1981; Jickells *et al.*, 1990; Shimmield and Pederson, 1990) where it is remineralized during organic matter decomposition as iodide to the porewaters (Kennedy and Elderfield, 1987a, b; Luther *et al.*, 1995).

2. Materials & Methods

The approach detailed by Truesdale and Moore (1992) was used throughout. Thus in principle, apparent iodine $\{\sum I_2 \text{ species}\}$ was determined by adding excess potassium iodide to form I_3^- and measuring the absorbance, and apparent iodate $\{\sum I_2 \text{ species plus iodate}\}$ was determined by the same method after acidification to convert iodate to I_2 species. Absorbance was measured at 285 nm using a Milton-Roy Spectronic 601 spectrophotometer equipped with 10 cm quartz cuvettes. ACS reagent grade reagents were used throughout. The reduction of M.I. in seawater

TABLE I. The iodine species considered for the determination of I₂ transformations in seawater over the pH range 4-10 using the program MINEQL.

1)	I _{2(aq)}	+ H ₂ O	→	HOI + H ⁺ + I ⁻	log K ₁ = -12.26
2)	HOI	↔	H ⁺ +	IO ⁻	pK _a = 11; log K ₂ = -11
3)	I _{2(aq)}	+ I ⁻	→	I ₃ ⁻	log K ₃ = 2.86
4)	I _{2(aq)}	+ Br ⁻	→	I ₂ Br ⁻	log K ₄ = 1.2
5)	I _{2(aq)}	+ Cl ⁻	→	I ₂ Cl ⁻	log K ₅ = 0.17
6)	3 IO ⁻	→	IO ₃ ⁻	+ 2 I ⁻	log K ₆ = 20.27

Data for reactions 3, 4, 5 from Hogfeldt (1982)

Data for reaction 1 from Palmer and Lietzke (1982)

Reaction 6 calculated from free energy data (Stumm and Morgan, 1981)

pK_a from Stanbury (1989)

was carried out in 50 ml, glass-stoppered pyrex conical flasks (C.S. Glass, Malaga, N.J., U.S.A.).

The oceanic seawater used in this study was collected from 20 m depth at 35° 40'W, 72° 18'N (on the eastern side of the Gulf Stream) using a 10 L Go-Flo bottle. The Menai Straits and Delaware Bay samples were collected by bucket, vacuum filtered through a 1.0 μm Whatman GF/C glass-fibre filter which had been washed with 500 ml of de-ionised water, and used immediately.

Stock artificial seawater (19.0‰ Cl) was prepared by dissolving sodium chloride (31.5 g) in de-ionised water and making up to 1 L. Its pH was adjusted to about 8.1 by adding sodium carbonate (2 × 10⁻⁴ M) and sodium hydrogen carbonate (2 × 10⁻³ M). In anticipation of experimentation on a given day, a 12 L batch of artificial seawater was prepared and then treated overnight with saturated M.I. solution (approximately 45 ml). Immediately before use, each batch of working solution was analysed for apparent molecular iodine to ensure that it contained a residual concentration of 1.5–2.0 μM M.I. Note that an apparent iodate measurement is useless for this purpose as disproportionation to iodate can occur in batches with pH approximating that of seawater, or higher, and the measurement may give a false impression of there being M.I. present.

Iodine speciation in seawater was calculated with the aid of an interactive version of the thermodynamic program MINEQL (Westall *et al.*, 1976).

3. Results & Discussion

3.1. SPECIATION OF M.I. ADDED TO SEAWATER

As our further experiments with the organic compounds spanned the pH range 4–9 it has been necessary to establish the concomitant changes in iodine speciation. It is convenient to describe these briefly before considering the reduction process. The iodine species [I⁻, I₂, I₂Cl⁻, I₂Br⁻, I₃⁻, HOI, OI⁻, IO₃⁻] were considered, and Table I shows the equilibria for these species with literature constants used.

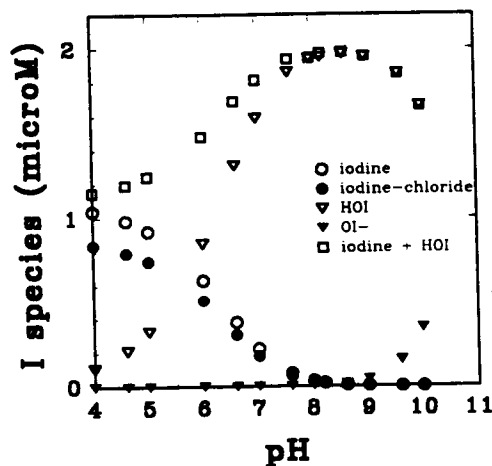


Fig. 1. The variation with pH of the speciation of iodine in seawater to which $2 \mu\text{M}$ of I_2 has been added; neglecting the formation of iodate.

Figure 1 shows the results of our thermodynamic modelling [calculated with the thermodynamic program MINEQL (Westall *et al.*, 1976)]. The results are generally consistent with those of Palmer and Lietzke (1982) while also including the minor interhalogen species. Iodate formation is not considered in Figure 1 because the reduction reaction is faster than disproportionation for molecular iodine.

The thermodynamic modelling indicates that when $2 \mu\text{M}$ of M.I. is added to seawater the major iodine species available for reaction with organic matter are HOI which increases with increasing pH, and I_2 and I_2Cl^- which decrease with increasing pH. HOI is a significant species over the entire range of 4–10 and until OI^- predominates at very high pH values. It is identical in concentration to the iodide (not plotted) because equimolar amounts of HOI species and I^- are formed on hydrolysis of I_2 ; this hydrolysis reaction occurs in less than a second (Eigen and Kustin, 1962). I_2Cl^- is a significant species from pH 4–7 and is 80% of the I_2 concentration. The other anions, I_3^- and I_2Br^- , are calculated to be 0.5% of the M.I. originally added at pH 4. Both I_3^- and I_2Br^- decrease with increasing pH and are insignificant at pH >4. The concentration of the hypiodite anion, OI^- , only becomes important at pH values above that of seawater; at pH 8 it represents only about 0.25% of the M.I. added originally. At low pH values, such as those found environmentally in salt marsh porewaters (Luther *et al.*, 1991b and references therein), I_2 is likely to be the primary reactant because it is an electron acceptor and I_2Cl^- is not; there HOI is not present in significant quantities.

3.2. SCREENING EXPERIMENTS IN ARTIFICIAL SEAWATER – pH 8.2

We have conducted screening experiments which confirm that amino-N compounds, activated aromatic compounds, and compounds with α -keto carbon-hy-

TABLE II. The compounds tested, showing the fraction (%) of approximately 2 μM of M.I. reduced after 1, 12 and 24 hours, respectively, by a concentration of 100 μM of compound.

Functional Group	Compounds	Fraction reduced after given period		
		1 hour	12 hours	24 hours
Amino acids	Glycine, Alanine, Phenyl-alanine, Asparagine, Glutamine		23	46
			100	
Amino acid with aromatic moiety	Tyrosine, Histidine	100		
Simple aromatic compounds	Phenol, Salicylic acid Pyrrole Phthalic acid Benzoic acid	100		
			16	23
			0	0
Unsaturated compounds	Fumaric acid Maleic acid Acrylic acid		3	9
			2	4
			11	12
Carbonyl compounds with adjacent -H atoms	Pyruvic acid, α -ketoglutaric acid Ascorbic acid 2-keto-gluconic acid 5-keto-gluconic acid Oxalacetic acid	100		
		100		
		100		
			18	38
			100	
Simple carbonyl compounds	Acetone Acetaldehyde Glyoxylic acid		83	
			100	
			22	25
Simple amines and amides	Urea Guanidine Ethyl diamine Di-ethylamine		7	12
			0	0
			40	40
			83	
Carboxylic acids	Lactic acid Propionic acid		5	6
				100
Complex pyrrole (aromaticity)	Vitamin B ₁₂		4	4
Poly-peptide	Glutathione (oxidised form)	100		
Polysaccharide	Dextrose		46	69

drogen groups at a concentration of 100 μM (the approximate concentration of DOC in seawater) will reduce M.I. (approx. 2 μM) added to artificial seawater (Table II). Although disproportionation can occur, we did not measure significant amounts of iodate as a product in selected systems tested. In the Gulf Stream water

sample, iodate was finally detected at room temperature after one week of reaction. In every case a blank determination was performed by carrying the original iodine solution through the entire experiment and the loss of M.I. from the blank solution was generally appreciably smaller (< 5%) than the loss occurring with the test compound. These same tests showed that reduction of M.I. by the available alkene compounds was appreciably slower. Indeed, the amount of reduction was sufficiently small to have been attributable to an impurity, rather than the parent compound. The alkenes tested were chosen because of their known chemistry in seawater; e.g., acrylic acid results from the breakdown of dimethylsulfoniopropionate (Vairavamurthy and Mopper, 1987). For acrylic acid, the pK_a is 4.25 so the anion predominates under our experimental conditions. The highest occupied molecular orbital in these alkenes is the carboxylic acid group and not the olefinic group based on semi-empirical molecular orbital calculations using the commercially available program HYPERCHEM. Thus, M.I. species will interact with the anion group which is a better electron donor group than the olefinic group. If the simple alkenes did actually reduce M.I. a mono-iodine compound would have been formed because at pH 8.2 the major iodine species present is HOI not I_2 . This is different to the direct addition of an I_2 molecule (Ingold, 1963). Moreover, in polar solvents, electrophilic attack by the halogenating agent yields a carbonium ion intermediate which is subsequently attacked competitively by the negative ions in solution. In seawater these are chloride and hydroxide, and mixed chloro-iodo compounds as well as iodohydrins, i.e., iodo-alcohols, can be expected.

Reaction with the straight-chain amino compounds probably reflect the formation of iodamines, $R(R')N-I$ from primary or secondary amines, amino-acids, and amides (Noller, 1966), as deduced from the corresponding chlorine chemistry (Alouini and Seux, 1987). Thus, the N-chloramines of amino acids decarboxylate spontaneously, to yield carbon dioxide, chloride and an imine ($C=N-R$) compound. The imine subsequently decomposes to an aldehyde and primary amine, which then reacts to produce another chloramine. Overall the reaction involves production of Cl-N bonds in simple chloramines. Assuming iodine follows the same pattern the aldehyde, iodamine and iodide can be expected as products. The paucity of added M.I. eliminates the need to consider di-iodamine formation which might occur at higher concentrations. In any case, the iodine atoms may well be too bulky to allow di-iodamine formation.

Although pyrrole is another (weak) N-base containing an N-H group its aromatic character dominates its reaction with iodine and tri-iodopyrrole (iodole) is produced through ring substitution. Similar aromatic substitution in the imidazole ring present in the amino acid, histidine, is responsible for its rapid reaction with M.I. (Schofield *et al.*, 1976). This aromatic effect is also witnessed in the production of radio-labelled proteins for biochemical studies. Thus, Bailey (1990) states that the iodinating reagent (iodide plus a "mild" oxidising agent such as peroxide or chloramine-T) introduces a radio-iodine atom into an aromatic nucleus (tyrosine or histidine) well before the spine of the protein is attacked.

Likewise, benzene derivatives, depending upon their degree of aromatic activation by existing substituents, iodinate. Benzoic acid appeared inert as anticipated from the presence of the deactivating COOH group. However, the inclusion of the activating hydroxyl group, in salicylic acid, more than compensated for this. Phenol, of course, is known to react with iodine and has been used to remove excess iodine in analytical work on iodate in seawater (Truesdale, 1978). Phthalic acid, with its additional "de-activating" carboxyl group was expected to be more inert than benzoic acid, but proved otherwise.

Propionic acid was also an unexpected addition to the list of reducers. Acetic acid has been used in micro-iodimetry without reacting with iodine (Barkley and Thompson, 1960) and so it was assumed that propionic acid, its near homologue, would behave similarly.

All the keto-compounds tested reduced M.I. Many contained carbonyl groups adjacent to a methyl group. This configuration makes the hydrogens of the methyl group more acidic, and base-promoted (N.B., not catalysed) carbanion formation is possible (Noller, 1966). The carbanion is stabilized by the existence of an enolic tautomer thereby facilitating electrophilic substitution by a positive iodine from I_2 or HOI. If the methyl group is terminal, further substitution on this same C-atom occurs because the inductive effect of the introduced iodine atom makes the remaining hydrogens even more acidic. Finally, cleavage occurs producing triiodomethane, i.e., iodoform, and a carboxylic acid. Indeed, overall this is the well documented "iodoform reaction". In contrast, where up to two of the hydrogens of the methyl group are already substituted, a mono-iodo derivative results and there is no cleavage to form iodoform. These reactions therefore result in the production of C-I bonds.

The difference in rate of reduction for the 2- and 5-keto gluconic acids is noteworthy. The inductive, electron withdrawing effect of the carboxyl group on the carbonyl group's ability to enolise in the 5-keto isomer appears to be akin to that in pyruvic and α -keto glutaric. However, moving the carbonyl to the 2-position where it is adjacent to C-atoms containing hydroxyl groupings slows the reaction considerably.

The aldehyde group of glyoxylic was probably oxidised to form oxalic acid, which itself is oxidised to carbon dioxide and water by M.I. (Morgan, 1954). Reduction of M.I. by this route produces iodide. Dextrose, as an aldo-hexose probably follows a similar reaction, to be converted to D-gluconic acid.

3.3. VARIATION IN REDUCTION RATE WITH pH FOR SPECIFIC COMPOUNDS

With salicylic acid and α -keto-glutaric acid, plots of $\log(A_t - A_\infty)$ versus time (i.e., semi-log plots) were linear for at least 75% of the reaction, and typically, with between 14 and 20 points correlation coefficients close to 1.0 were obtained ($r^2 \geq 0.982$). This is consistent with the kinetic behaviour of other similar compounds and is succinctly described by

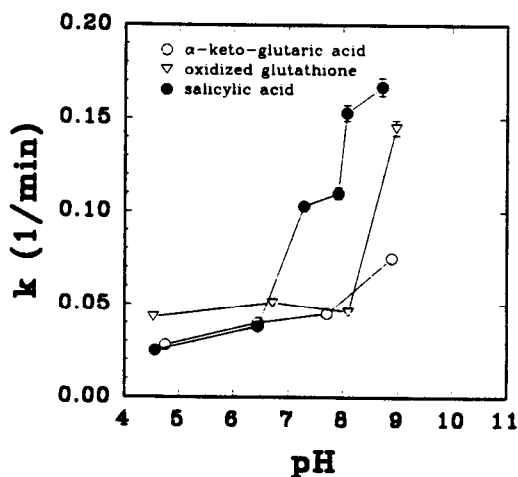


Fig. 2. Rate constant versus pH data for the reaction of M.I. with α -ketoglutaric acid, oxidized glutathione and salicylic acid.

$$\text{velocity} = \frac{d[\Sigma I_2]}{dt} = k_{\text{OBS}} \cdot [\Sigma I_2] \quad (1)$$

The variation with pH of the pseudo-first order rate constant, k_{OBS} , for reduction of M.I. by these two compounds is shown in Figure 2.

The reaction between added M.I. and the oxidized form of glutathione (RS-SR) did not follow either simple first or second order behaviour. However, semi-log plots were linear after the first five or so minutes of reaction. With our limited objective of obtaining a pH fingerprint for the reduction by each compound, we have used the gradients of the linear part of each semi-log plot to gauge the variation of the rate with pH change (Figure 2).

3.3.1. Salicylic Acid

We have modelled the kinetics of reduction of M.I. by salicylic acid assuming equilibrium between the iodine species, I_2 , I_3^- , HOI and IO^- and iodination via two reactions, first order in either HOI or I_2 . The assumption of a pre-equilibrium of iodine species is reasonable as, at 25 °C the iodination reactions take many minutes whereas iodine speciation re-adjusts within a fraction of a second (Eigen and Kustin, 1962). Thus, mechanistically the rate can be reasonably assumed to be given by

$$\text{velocity} = k_a \cdot [I_2] \cdot [\text{Sal.}] + k_b \cdot [\text{HOI}] \cdot [\text{Sal.}] \quad (2)$$

where k_a and k_b are rate constants, and [Sal.] is the concentration of salicylic acid. Simultaneous application of (2), the equations for the equilibrium constants K_1 , K_2

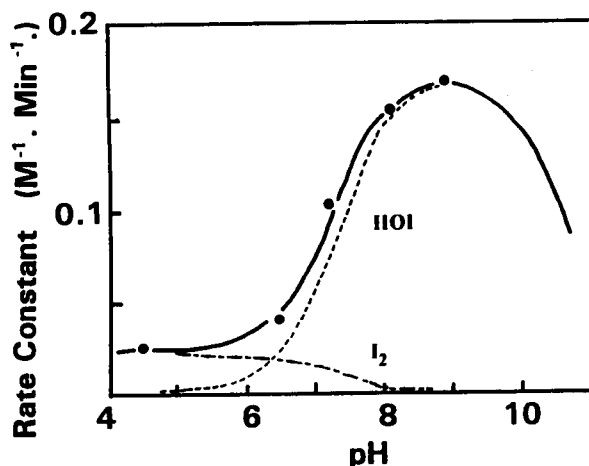


Fig. 3. The variation in the experimentally and predicted rate constant for reduction of M.I. by salicylic acid. The broken lines indicate the separate contributions from reaction with I_2 and HOI. HOI is the predominant reactant above pH 6.50.

and K_3 from Table I for the I_2/HOI , HOI/IO^- and I_2/I_3^- equilibria, and the mass continuity equation

$$[I_2] + [I_3^-] + [HOI] + [IO^-] = [\Sigma I_2],$$

lead to

$$\text{velocity} = \frac{[\Sigma I_2] \cdot [\text{Sal.}]}{\alpha} \left[k_b + \frac{k_a \cdot [I^-] \cdot [H^+]}{K_1} \right] \quad (3)$$

where

$$\alpha = \left[1 + \frac{[H^+] \cdot [I^-] (1 + K_3 \cdot [I^-])}{K_1} + \frac{K_2}{[H^+]} \right].$$

Comparing the coefficients of (1) and (3) gives

$$\bar{k}_{OBS} = \frac{[\text{Sal.}]}{\alpha} \left[k_b + \frac{k_a \cdot [I^-] \cdot [H^+]}{K_1} \right] \quad (4)$$

where \bar{k}_{OBS} is the value of k_{OBS} predicted by the model.

The close agreement between the variation with pH of the predicted and experimentally measured rate constant k_{OBS} is shown in Figure 3. The rate constants k_a and k_b are used to scale the relative contribution of each of the two components of the reaction (2), while the iodide concentration controls the position of the left-hand slope of the curve. The best fit of experimental (solid line) and predicted results required an iodide concentration of 10^{-5} M whence k_a and k_b were 0.022 and $0.17 \text{ M}^{-1} \text{ min}^{-1}$, respectively. Although the actual iodide concentration was not

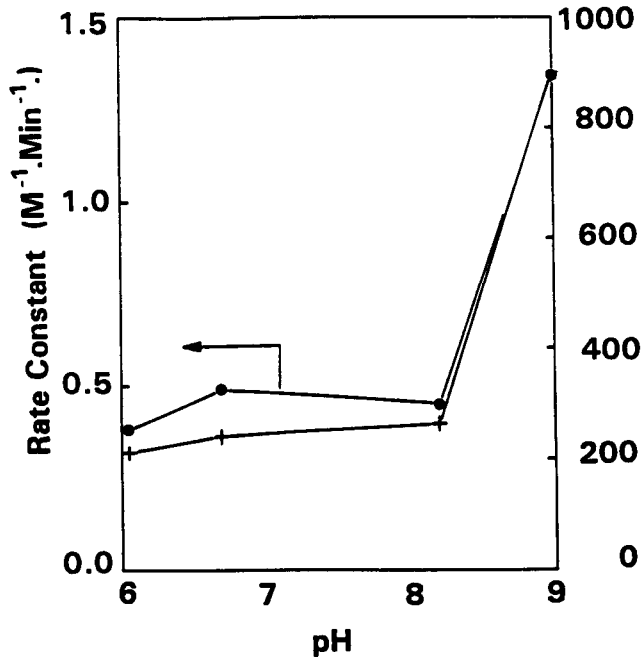


Fig. 4. The variation of the rate constant for reduction of M.I. by natural substances in Menai Straits seawater. Rate constants measured by fitting the model of Truesdale *et al.* (1995) to the raw data. (+) k_1 (right scale); (•) k_2 (left scale).

to the increased proportion of “free” amino group as well as hydroxyl attack on hydrogens α - to the keto groupings. Where the HOI concentration increases (pH 4 to 8) the rate constants for the oxidised glutathione changed relatively little. Thus, as with α -keto glutaric acid, I_2 and HOI are equally effective as electron acceptors in reaction with the functional groups of oxidised glutathione.

3.4. VARIATION WITH pH OF THE REDUCTION RATE IN REAL SEAWATER

The variation with pH of the rate of reduction of M.I. in a sample of Menai Straits water at 25°C is shown in Figure 4. The rate constants of Figure 4 were obtained by fitting experimental data to the model described by Truesdale *et al.* (1995), which allows for a rapid total consumption of one set of organic compounds (k_1) and a more sustained consumption of a second group (k_2), all first order in respect of the organic components. It can be seen that the two rate coefficients varied in the same way toward changes in pH. Between pH 6 and 8 the rate constants were constant but increased markedly at pH 9.0. A similar result was obtained using a sample of Delaware Bay water.

Oceanic water was also found to behave similarly. These reactions were performed at 50°C to obtain a faster reaction since at room temperature the reaction takes up to a week. Thus, the kinetic curves for samples of oceanic seawater (Fig-

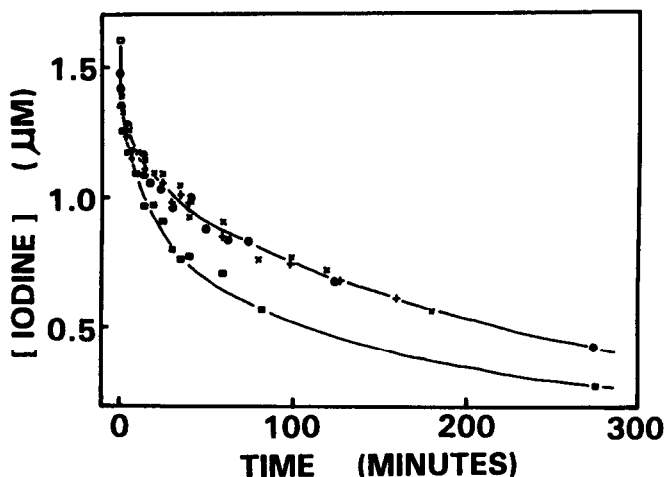


Fig. 5. The reaction curves for reduction of M.I. by naturally occurring substances in oceanic seawater, at 50°C. (x) pH 5.05, (+) pH 7.2, (•) pH 8.22, (■) pH 9.0.

ure 5) and pHs 5.05, 7.20 and 8.22 were indistinguishable from one another while that for pH 9.05 was appreciably faster.

4. Discussion

The marked change in the pH fingerprint of the reduction of M.I. in natural seawater between pH 8 and 9 (Figures 4 and 5) is similar to the pH fingerprint for oxidized glutathione and α -keto-glutaric acid (Figure 2), and confirms Truesdale's (1993) tentative observation. The pH change in seawater suggests that the overwhelming effect is of hydroxide ion involvement as with α -keto glutaric acid and glutathione. Simple changeover of I_2 to HOI with increasing pH does not appear to have the same effect as it does with salicylic acid, because the greatest change in iodine species occurs below pH 8. The kinetics do not change from pH 4 to 8 for natural organic compounds in seawater, α -keto glutaric acid and glutathione (Figures 2 and 4). Between pH 8–9, HOI is the dominant chemical form (see Figure 1) and does not dissociate significantly indicating that the electron acceptor activity does not change over this pH range. Indeed, the constancy of the rate coefficients for natural organic material in seawater with decrease in pH below 8 actually shows an indifference to changeover in speciation to I_2 from HOI. Simple alkenes did not react as efficiently with M.I. over the pH range studied as do the above compounds with α -keto groups involved in keto-enol tautomerism. On this evidence, α -keto groups and amino groups are likely functional groups for the observed reaction of M.I. with natural organic matter in seawater. This result with model organic compounds appears to agree with our knowledge of organic carbon and nitrogen in seawater as discussed below.

The distribution of organic compounds and their functional groups in seawater has been the subject of much discussion (e.g., Lee and Wakeham, 1988). Recently, Benner *et al.* (1993) have used ^{13}C NMR to estimate the number and types of carbon compounds in seawater. They concluded that polysaccharides can make up to 50% of the carbon in dissolved organic matter (DOM) in surface seawater whereas carbonyl, carboxyl and ester carbon make up about 20%, and aromatic and olefinic carbon makes up < 10%. These results appear consistent with the measurements made by several workers on carbonyl compounds. For example, Mopper and Stahovec (1986) and Kieber *et al.* (1990) have shown that simple carbonyl containing compounds exist in concentrations of 100 nM or less, but can be produced rapidly and transiently by breakdown of polymeric material via UV excitation in surface seawater.

In addition, Benner *et al.* (1993) found that the C/N ratio of dissolved organic carbon in surface seawater is near 15. In their surface samples, total dissolved organic carbon was about 80 μM which indicates that total dissolved nitrogen in DOM is about 5.3 μM . In our experiments the M.I. added is 2 μM or the total iodine added is 4 μM . Thus, the general distribution of free amino acids, peptides and proteins in seawater should provide an M.I. sink equivalent to a few μM each of amine-N and carbonyl-C (with α -keto groups).

I_2 has also been invoked in processes which lead to enrichment of I relative to Cl in maritime air and rainwater (e.g., Miyake and Tsunogai, 1963). It appears from the collected work on M.I. reduction that organo-I compounds with both C-I and N-I bonds will be formed in any waters that liberate I_2 , as the reduction reaction competes with HOI disproportionation to IO_3^- , and with I_2 volatilization. Therefore, the identification of organic-I compounds under appropriate oceanic circumstances might well offer evidence for sites of molecular iodine generation, and indeed, some measure of their fluxes. Dissolved organic-I is generally present at low but measureable concentrations in inshore regions and enclosed anoxic basins (< 100 nM; Luther and Campbell, 1991; Luther *et al.*, 1991a; Truesdale, 1975; Ullman *et al.*, 1990). Thus, it is conceivable that a micro-chemistry of organic-I compounds at even lower concentrations might well exist in open ocean surface waters, as does that for carbonyl compounds (Kieber, *et al.*, 1990). Whether such a microchemistry can be discovered *in situ* will depend much upon the rates at which iodo compounds are hydrolysed either abiologically by hydroxide in seawater by the classical $\text{S}_{\text{N}}1$ or $\text{S}_{\text{N}}2$ substitution reactions (Noller, 1966; Ingold, 1963), or microbially. In both cases iodide will result. Thus, there is some merit in investigating the abiotic and biotic hydrolysis of likely organo-I compounds. This approach of studying the reactivity of known intermediates has been used with success in water chlorination studies (e.g., William and Wendy, 1979) where, of course, Cl-N bonds are of interest. The identification of a dissolved iodine microchemistry will also depend upon its being discernible against the background of the conventional bio-cycling of iodine as well as the production of iodo-alkanes of biogenic origin (Klick and Abrahamsson, 1992).

Evidence for an organic I microchemistry is provided by particulate flux from surface waters to the sediments. Particulate organic iodine is formed in surface waters of the ocean by incorporation into organisms which are transported to oceanic sediments (Deuser *et al.*, 1981; Jickells *et al.*, 1990; Shimmield and Pederson, 1990). Biotic decomposition of organic matter which contains C-I and N-I bonds (Harvey, 1980; Upstill-Goddard and Elderfield, 1988) in sediments releases iodide into porewaters at micromolar levels which are above the total oceanic iodine concentration of 0.5 μM (Kennedy and Elderfield, 1987a, b; Luther *et al.*, 1995). Decomposition of particulate material also occurs in the water column (Lee and Wakeham, 1988) and is indicated when the total iodide concentration and/or the total iodine to salinity ratio increases over normal oceanic values (Luther and Campbell, 1991; Luther *et al.*, 1991, 1995).

5. Conclusions

Using a combined thermodynamic and kinetic modelling approach, the reaction of molecular iodine species with model organic compounds in seawater has been studied over the pH range 4–10. Above a pH of 8, the modelling results indicate that HOI is the primary iodine reactant for all organic compounds. Aromatic compounds react faster than all other organic compounds at seawater pH; α -keto compounds and peptides have lower reactivity at seawater pH and increase in reactivity at pH 9. The slowest organic reactants were the alkenes tested. The pH “fingerprint” studies indicate that α -keto compounds and peptides are the likely organic compounds reacting with molecular iodine species in natural seawater. These compounds incorporate iodine as C-I and N-I bonds resulting in a significant organic I chemistry.

Acknowledgements

This work was supported by a grant from the National Science Foundation to GWL (OCE-9217245). We thank Anna Farrenkopf and Jody Stecher for their aid in the laboratory. V.W.T. also thanks Anna, Jody, and the other members of the staff of the College for making his visit so memorable. V.W.T. also wishes to thank Peter Foster and Sylvia East of the Ocean Sciences Dept., University of Wales, for providing bench space in which to analyse the Menai Straits samples.

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