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The chemical reduction of molecular iodine in seawater*

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Abstract—Molecular iodine is shown to be unstable in seawater. Eighty-five per cent of 1400 μg l^{-1} of I_2-iodine added to an inshore seawater was chemically reduced within the first 24 h of reaction at 30°C. Organic matter present in the seawater is believed to be responsible for this chemical reduction of molecular iodine. The results suggest that at least two reduction reactions proceed simultaneously. The rate of conversion of molecular iodine to iodate and iodide by disproportionation of hypo-iodite was slow in comparison. With higher initial molecular iodine concentrations production of iodate was observed.

1. INTRODUCTION

THE HYDROGRAPHIC surveys conducted by SUGAWARA and TERADA (1957), BARKLEY and THOMPSON (1960), TSUNOGAI (1971) and LISS, HERRING and GOLDBERG (1973) have shown that the total iodine content of most seawaters is between 40 and 60 μg l^{-1}. Further, they have shown that the ratio of the concentration of the two forms of iodine known to exist in seawater, iodate and iodide, varies spatially. In order to explain this variation, workers have proposed mechanisms which lead either to the reduction of iodate or the oxidation of iodide in the sea. The molecular iodine species, I_2, has often featured in the mechanisms although there is little or no evidence for its existence in natural seawater. Nevertheless, it has been a particularly attractive intermediate as the oxidation of iodide to molecular iodine requires a smaller free energy change than the oxidation of iodide to iodate. Also a proportion of any molecular iodine in seawater would be expected to be converted to iodate by a disproportionation reaction involving the hypo-iodite ion which molecular iodine readily forms in water at the pH of seawater.

$$\begin{aligned} I_2 + H_2O &= HIO + HI \\ HIO &= H^+ + IO^- \\ 3IO^- &= IO_3^- + 2I^- \ldots\ldots \text{(Disproportionation)} \end{aligned}$$

Although several workers, e.g. MIYAKE and TSUNOGAI (1963), SHAW and COOPER (1957, 1958), have presumed that molecular iodine is present in the seas, only SUGAWARA and TERADA (1958) seem to have tested its stability in seawater. They found that 50 mg of molecular iodine added to a litre of seawater (that is, a 1000-fold increase in

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*One of the referees queried the use of the word 'reduction' which was used in the original title and throughout the paper. He felt unsure whether 'chemical reduction' was indeed being discussed. The author decided, after deliberation, to retain the word 'reduction', and nevertheless has qualified it, on occasion, to 'chemical reduction'.—Note by Editor.

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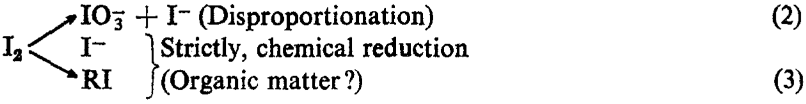
total iodine concentration) was converted to iodate and iodide via the disproportionation of hypoiodite during a period of 25 days. A study of the marine chemistry of iodine conducted in these laboratories demonstrated that molecular iodine in seawater is involved in at least one other reaction sequence. This sequence is presumed to involve the oxidation or iodination of organic matter dissolved in seawater. As this reaction competes effectively against the disproportionation reaction it is probably of great importance in the iodine cycle of the oceans. This paper describes the results of some investigations of this reaction.

2. EXPERIMENTAL

Molecular iodine in seawater can (1) remain unchanged, (2) undergo disproportionation or (3) be chemically reduced.



$$\mathrm{I_2}\begin{array}{l}\nearrow \mathrm{IO_3^-} + \mathrm{I^-}\ \text{(Disproportionation)} \qquad (2)\\ \left.\begin{array}{l}\rightarrow \mathrm{I^-}\\ \searrow \mathrm{RI}\end{array}\right\}\begin{array}{l}\text{Strictly, chemical reduction}\\ \text{(Organic matter?)}\end{array} \qquad (3)\end{array}$$

The sum of the I_2 and IO_3^- obtained by the first two reactions (the apparent molecular iodine concentration) is estimated by the analytical method used; the iodate formed by disproportionation being re-converted to molecular iodine under these analytical conditions. The molecular iodine lost by chemical reduction can therefore be obtained by difference, initial levels of molecular iodine being known.

Possible alternative explanations for the observed loss of molecular iodine were excluded. Thus, the extent of the loss did not vary when the geometrical surface area of the glass in contact with a given volume of mixture was doubled by means of 0·5-cm glass balls. Irreversible adsorption of iodine on the vessel walls can therefore be dismissed. Other tests showed that the total iodine concentration of the mixtures remained constant throughout the experimental period. The extent of any loss of molecular iodine by diffusion from the vessels was, therefore, insignificant.

Experimental procedure

Each seawater was filtered through a washed (250 ml of distilled water) Millipore® membrane filter (0·8 μm APD) immediately before molecular iodine was added. Most of the oxygen present in each sample was also removed at this time by bubbling oxygen-free nitrogen through for 30 min. The oxygen, which interferes with the titrimetric method used for oxidized-iodine determination, cannot be removed after treatment with molecular iodine as the nitrogen used also purges appreciable quantities of molecular iodine from solution.

Molecular iodine was added to seawater as a saturated solution in distilled water. This solution was standardized before use by titration against sodium thiosulphate (10^{-3} N) using starch as an indicator. Both neutral and acidic conditions were used during standardization in case a correction was necessary for any iodate present. Mixtures of iodine and seawater were stored in glass bottles fitted with tightly fitting ground glass stoppers. The bottles were held in a covered, thermostatically controlled water bath at 30 ± 0·5°C. After an allotted period a sample from each bottle was titrated. The titrimetric procedure described by TRUESDALE and SPENCER (in press) was used to estimate these low concentrations. When high concentrations of iodine were anticipated only 25 ml of each sample was taken as opposed to the usual 100 ml aliquot. This was mixed with 75 ml of de-ionized water from which oxygen had been removed in the manner described above. A sample of each seawater tested was analysed before addition of iodine in order to establish the "iodate-blank" produced by the naturally occurring iodate-iodine. Total iodine was determined by means of the automatic procedure also described by TRUESDALE and SPENCER (in press).

3. RESULTS AND DISCUSSION

Tests conducted on several seawaters, taken throughout one year from the Menai Straits, have shown that molecular iodine added to seawater undergoes reduction rapidly. The smallest amount of molecular iodine added to any sample during these tests should have given a solution of 260 $\mu g\ l^{-1}$, I_2-I. However, after only 30 min this solution apparently contained no molecular iodine. This observation shows that the removal process is very fast even at concentrations of iodine that approach those found naturally. It supports the belief that significant concentrations of molecular iodine will not occur in the oceans. The rate is approximately thirty times higher than the rate of uptake of iodide by *Laminaria* sp. as observed by SHAW (1959, 1960), hitherto the most rapid iodine interconversion reaction reported for a marine system.

During this work it has not been possible to determine the nature of the other reactants involved in this process. Nevertheless, it seems unlikely that inorganic materials would be present in sufficiently large concentrations to cause the observed changes. Further, addition reactions where molecular iodine attacks unsaturated carbon bonds in lipids and hydrocarbons, are well known. Also, molecular iodine can oxidize some carboxylic acids, e.g. oxalic acid, to carbon dioxide. As members of these three groups of compounds exist in seawater (HOOD, 1970), it is reasonable to suppose that they are responsible for the observed chemical reduction process.

An examination of the kinetics of this chemical reduction of molecular iodine has revealed a complex situation best rationalized by postulating two reaction types. The results, Table 1, obtained using three initial concentrations of molecular iodine, showed that a precipitous fall in the apparent molecular iodine concentration was followed by a more gradual one. The average rate of chemical reduction of molecular iodine during the first half-hour interval of reaction was approximately 21 $\mu g\ l^{-1}\ min^{-1}$, in each case. During the second half-hour interval it was at most $\frac{1}{5}$th this magnitude. At least 85% of the added molecular iodine was reduced within 24 h. This appears to indicate the presence of a reducing agent whose concentration is exhausted after about half an hour. This would explain why the rate of chemical reduction at a fixed apparent molecular iodine concentration can be so different in the three cases studied. It appears, therefore, that a reaction which runs speedily to equilibrium proceeds concurrently with a slower reduction process. Characterization of the slower reduction reaction (after 30 min) in terms of its order with respect to molecular iodine was inconclusive. Correlation coefficients consistently greater than 94% were obtained for the regression of both the reciprocal and logarithm of molecular iodine concentration on time. However, inconsistencies in the calculated velocity constants indicated a more complex reaction than that described by first or second order kinetics.

Experiments have shown that the overall behaviour of molecular iodine in seawater varies with its initial concentration. Tests were conducted on several seawaters by adding various known amounts of molecular iodine to aliquots of each filtered

Table 1. *The chemical reduction of molecular iodine in seawater.*

Mixture	*Apparent molecular iodine concentration* (μg l⁻¹, I₂-I) *after given reaction period* (h)							
	0	0·5	1·0	1·5	2·0	2·5	3·0	24
I	1400	770	630	550	470	420	370	216
II	980	330	250	190	160	130	—	97
III	700	95	90	85	80	—	—	67

seawater. The mixtures were incubated for more than two weeks before analysis. Graphs of the amount of molecular iodine chemically reduced, against the amount added, were drawn. These showed that the previously mentioned behaviour held when between 0 and 2·5 mg l^{-1} of molecular iodine was added. The gradient of each graph was constant over this range and greater than 0·9. It is not known whether the residual oxidized species (< 10%) were in the form of molecular iodine or iodate-iodine formed by the disproportionation reaction. Nevertheless, it is clear that in inshore waters the reduction process exerts a far greater effect on molecular iodine than the disproportionation reaction. When initial molecular iodine concentrations greater than 3 mg l^{-1} were administered, the proportion of molecular iodine chemically reduced was smaller. The reduction process was not satiated, however, even by approximately 13 mg l^{-1} of molecular iodine. The gradients of the removal versus addition graphs relating to the six seawaters tested, were constant and equal to 0·15 (± 0·01) over the range 3–13 mg l^{-1} of added molecular iodine. The change in the pattern of behaviour at about 2·5 mg l^{-1} of molecular iodine suggests that one component, or one group of components, of seawater is completely oxidized or iodinated by this amount of molecular iodine. This reducing capacity of 10^{-5} N for seawater is of the same order as that found by KORRINGA and POSTMA (1957) when they used alkaline permanganate to measure the dissolved organic matter in Gulf of Naples water. The similarity between these figures lends credibility to the postulate that organic matter is responsible for the observed reduction of molecular iodine in seawater.

The preceding results show that iodate production, by disproportionation of hypo-iodite, only occurs to a significant extent after the reduction reaction is completed. Other tests, of a qualitative nature, showed that iodate was formed when the high initial molecular iodine concentrations were used, thus adding further support to this contention. There is, therefore, no contradiction between the observations made by SUGAWARA and TERADA (1958) and those made here. The production of iodate and iodide, via disproportionation of hypo-iodite, would be expected after 50 mg l^{-1} of iodine had been added. Also, it is probable that the extent of any chemical reduction in Sugawara and Terada's experiments was too small to be detected by the analytical method they used.

The observations described above were made whilst using filtered Menai Straits water. The use of unfiltered water which contains an additional organic load might be expected to increase the rate and extent of iodine reduction. Therefore, the *in situ* rate of molecular iodine reduction in coastal waters might well be greater than that recorded here. Insufficient data is available to allow a realistic extrapolation to oceanic waters. Nevertheless, because of the smaller organic content, the rate of reduction of molecular iodine in oceanic water is probably lower than that recorded here for filtered coastal water. Spatial and temporal variation in the rate and extent of reduction of molecular iodine by seawater is therefore to be anticipated.

It is interesting to examine the implications of the reduction reaction on our general understanding of the marine chemistry of iodine. Clearly, whenever molecular iodine is invoked as an intermediate in a marine chemical reaction sequence, interference by the reduction reaction must be suspected. Therefore, in studies of the other reactions of molecular iodine in seawater, e.g. disproportionation, it will be advisable to reduce uncontrolled variation of this interference which will arise from the use of different seawaters. This seems especially so when experiments are performed using both natural and artificial seawaters. The reduction reaction will compete with other reaction sequences in which molecular iodine is involved and which lead to production of other iodine species. The rate of molecular iodine production will, therefore, have to be appreciably greater than the overall rate of formation of the other iodine species. Examples of such sequences are found in the uptake of iodine by *Laminaria digitata* (SHAW, 1959) and enrichment of the atmosphere with molecular iodine derived from the oceans (MIYAKE and TSUNOGAI, 1963). In the former case, molecular iodine is believed to be produced in an extra-cellular enzymatic reaction involving iodide; in the atter case, a photo-chemical reaction involving oxygen, iodide and ultra-violet light liberates molecular iodine. A re-appraisal of the results of such work will be necessary, therefore, if the iodine reduction reaction is found to operate universally. In the case of inshore waters, it is extremely unlikely that a significant amount of molecular iodine will cross from the sea to the atmosphere.

4. CONCLUSION

Molecular iodine is an extremely unstable form of iodine in coastal waters, and probably also in oceanic waters. In the waters tested the rate of chemical reduction of molecular iodine greatly exceeded the rate of its conversion to iodate-iodine. The reaction can only be studied successfully by augmenting the total iodine content of seawater with extremely small amounts of molecular iodine (10^{-6} M), because a different behaviour is associated with higher concentrations. This probably explains why the reaction has not demanded attention earlier. Because previously the reduction reaction has not been recognized as important, in some cases the empirically determined interconversion rates for iodine species are likely to be in error. Where molecular iodine is involved in a marine chemical reaction sequence, the rates of production of molecular iodine are probably much greater than the overall rate of the reaction sequence.

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