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Reaction of Methyl Halides with seawater and marine aerosols

by Oliver C. Zafiriou

ABSTRACT

Methyl iodide is known to be formed biologically in seawater and has been postulated as the agent of iodine air-sea transport. Kinetic calculations and experiments demonstrate that methyl iodide reacts with chloride ion in seawater to yield methyl chloride approximately as fast as it exchanges into the atmosphere. In seawater, both methyl chloride and methyl iodide are slowly hydrolyzed to methanol and halide ions. The rate of trapping of I on sea-salt particles by reaction with atmospheric methyl iodide is shown to be too slow to account for the enrichment of the marine aerosol in I relative to seawater.

Kinetic approximations developed for this study also establish an approximate scale of relative reactivity for seawater constituents interacting with carbon compounds in second-order nucleophilic reactions: Cl$^-$ > HOH > (HCO$_3$-$ + Br$^- +$SO$_4^{2-}$).

1. Introduction

The atmospheric transport of iodine from the oceans to land is estimated to be about 100-fold larger than other I sources, such as rock weathering, volcanism, and fossil fuel combustion (Miyake and Tsunogai, 1963). Iodine is found in the atmosphere principally (60–80%) as a gas (Moyers and Duce, 1972). The marine aerosol I/Na ratio is enriched by $10^2$ to $10^4$ fold relative to seawater I/Na (Martens, 1973).

Neither the speciation of the iodine entering the atmosphere from the sea nor the injection process is known. Evaporation of chemically or photochemically produced I$_2$ has been considered repeatedly (Miyake and Tsunogai, 1963; Duce et al., 1965; Moyers and Duce, 1972), but I$_2$ cannot be the principal atmospheric species (Zafiriou, 1974). Transport of I-rich surface-active organic matter to the atmosphere by bubble-breaking is a second possibility (Moyers and Duce, 1972; Seto and Duce, 1973).

Recently, Lovelock et al. suggested that biological methylation of I in the sea yields methyl iodide (CH$_3$I) which evaporates, serving as “the natural carrier of iodine from the sea to the land”. They measured CH$_3$I in seawater and the marine atmosphere, finding quantities of methyl iodide rather similar to the “total gaseous I” concentration reported (at other locations) by Moyers and Duce; additionally, the
seawater/atmosphere concentration ratios were suggestive of a flux from the sea to the air.

If methyl iodide is formed in the sea, its escape to the atmosphere must compete with its reactions with seawater constituents. Such reactions might yield significant water mass tracers, or impose other conditions which serve to test the hypothesis that methyl iodide is the principal species of I entering the marine atmosphere. This paper examines some of these possible seawater-methyl iodide interactions.

2. Materials and methods

Reagent chemicals were utilized without further purification. Sargasso Sea surface water (S = 35.7/o/oo) was filtered through 0.2 µm Gelman cellulose acetate filters into autoclaved glass-Teflon containers, and stored at 10°C. Kinetic studies utilized quantitative head-space gas analysis of reactant and product vapors over <10⁻³ M (<0.2 x saturation, except for saturated NaCl solutions) solutions of methyl iodide stirred and thermostated in all-glass containers. These solutions were kept in the dark, and ~10⁻³ M chloroform was added as internal standard. The standard, reactant, and volatile product were separated by gas chromatography on an 8 m by 0.3 mm wall-coated OV-101 column at 23 ± 1°C and were detected by flame ionization. Averages of triplicate determinations of methyl iodide/chloroform peak intensity ratios were used as data points. Pseudo-first order rate constants were derived from linear plots containing at least six data points over 60–95% of the reactions (usually three half-lives).

The identity of the product, which yielded a gas chromatographic peak that grew as methyl iodide disappeared, was verified by mass spectroscopy. About 0.1 cm³ of head-space gas from a completely reacted seawater-methyl iodide mixture was injected into the capillary leak inlet of a Finnegan system 150 quadrupole mass spectrometer; authentic methyl chloride gas was introduced similarly. The background-corrected spectra were obtained by subtracting air-only background spectra, utilizing the Finnegan data-handling system.

When preliminary experiments showed that methyl iodide reacts with seawater at an appreciable rate, the number of additional experiments necessary was minimized by calculating which are the most reactive species in seawater. The reaction of methyl iodide was assumed to be a displacement reaction (as are 1–4 below), and the relative reactivities of water and the seawater anions were estimated by using the Swain-Scott (1953) equation:

$$\log \left( \frac{k}{k_0} \right) = sn$$

(1)

Equation (1) estimates empirically the rate constant ($k$) of second-order nucleophilic displacements ($S_N2$ reactions) on a variety of carbon compounds relative to the rate ($k_0$) at which the compound reacts with water itself in aqueous solution. The nucleophilic constant $n$ of water is defined as 0, and the sensitivity $s$ of methyl bromide to changes in nucleophilicity is defined as 1.00. This equation and derived $n$ values
Table I. Swain–Scott Nucleophilic reactivities towards Methyl Iodide in S = 35 per mille seawater.\(^a\)

<table>
<thead>
<tr>
<th>Nucleophile</th>
<th>Concentration, M</th>
<th>Relative reactivity(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOH</td>
<td>55</td>
<td>1.00</td>
</tr>
<tr>
<td>Cl(^-)</td>
<td>0.54</td>
<td>9.4</td>
</tr>
<tr>
<td>SO(_4^{2-})</td>
<td>2.8 × 10(^{-2})</td>
<td>0.33</td>
</tr>
<tr>
<td>HCO(_3^-)</td>
<td>2 × 10(^{-3})</td>
<td>0.29</td>
</tr>
<tr>
<td>Br(^-)</td>
<td>8 × 10(^{-4})</td>
<td>0.12</td>
</tr>
<tr>
<td>I(^-)</td>
<td>10(^{-7})(^c)</td>
<td>10(^{-3})</td>
</tr>
<tr>
<td>OH(^-)</td>
<td>10(^{-8})</td>
<td>&lt; 10(^{-3})</td>
</tr>
</tbody>
</table>

\(^a\) Swain and Scott, 1953; Hine, 1962.
\(^b\) The terms for fluoride, phosphate, nitrate and iodate are very small.
\(^c\) Tsunogai and Henmi, 1971.

predict \(k/k_0\) with an average deviation of 60% for reactions covering a span of 10\(^5\) in rate (Swain and Scott, 1953).

The equation was applied to sea water by approximating \(s = 1.00\) for methyl iodide and methyl chloride (\(s\) ranges from 0.7 to 1.4 for much larger variations in substrate structure (Swain and Scott, 1953). Although \(n\) values for borate and carbonate ion are not available, these ions are unlikely to contribute significantly to the nucleophilicity of sea water.

3. Results

Thermodynamic calculations show that at equilibrium in sea water the following reactions proceed at 25\(^\circ\)C, 1 atm., pH 8, [I\(^-\)] < 4 × 10\(^{-7}\) M (Tsunogai and Henmi, 1971).

\[
\begin{align*}
\text{CH}_3\text{I}(g) + \text{Cl}^-_{(aq)} &= \text{CH}_3\text{Cl}(g) + \text{I}^-_{(aq)} \quad (2) \\
\text{CH}_3\text{I}(g) + \text{Br}^-_{(aq)} &= \text{CH}_3\text{Br}(g) + \text{I}^-_{(aq)} \quad (3) \\
\text{CH}_3\text{Br}(g) + \text{Cl}^-_{(aq)} &= \text{CH}_3\text{Cl}(g) + \text{Br}^-_{(aq)} \quad (4) \\
\text{CH}_3\text{X}(g) + \text{H}_2\text{O}(l) &= \text{CH}_3\text{OH}_{(aq)} + \text{X}^-_{(aq)}; \quad X = \text{Cl}^-, \text{Br}^-, \text{I}^- \quad (5)
\end{align*}
\]

Methyl iodide is thermodynamically unstable in seawater and its chemical fate is controlled by kinetics. Swain-Scott estimates of the relative reactivities of seawater constituents, including the reaction partners indicated in (2)–(5) are given in Table I. Chloride ion is predicted to be the dominant reactive species, with water second and other anions of negligible importance. These estimates thus predict that methyl iodide in seawater will react predominantly by (2). Methyl iodide and the methyl chloride produced by (2) also react more slowly according to (5).

Preliminary experiments showed that methyl iodide reacts to completion in saturated sodium chloride solution in several days, liberating iodide ion; it is stable for days in distilled water. The loss of methyl iodide was accompanied by the growth of a product peak which was gas chromatographically identical to authentic methyl chloride.

More accurate rate measurements are given in the upper five lines of Table II,
and some typical experimental data is shown in Figure 1. Sodium chloride solutions of the same chlorinity as seawater exhibit the same reactivity, verifying that chloride attack is the principal reaction occurring. The methyl chloride produced by (2) was identified in a reacted seawater-methyl iodide solution by mass spectrometry; the parent ions at m/e 50 and 52 were found in the same abundance ratio in gas over this sample as in authentic methyl chloride (after small background corrections were made). Iodide ion was detected in less than stoichiometric amounts; it is partially air-oxidized or otherwise consumed on the experimental time scale.
The reaction of methyl halides with water is too slow at oceanographically interesting temperatures to measure conveniently. The rates for these reactions were calculated by extrapolation of the very accurate data of Moelwyn-Hughes (1938). The data extend over the 40–120°C range, and equations for the $T$ dependence are given by this author, so these rates should be quite accurate.

4. Discussion

The production of methyl iodide by several marine photosynthetic organisms has been verified (G. R. Harvey, personal communication, 1973), and if the hypothesis of Lovelock et al. (1973) is correct, the surface ocean is a major source ($4 \times 10^{10}$ metric tons per year) of methyl iodide. Some of this methyl iodide will exchange into the atmosphere, and some will react with seawater to form methyl chloride. As the methyl iodide source is presumed to be photosynthetic, we approximate that the euphotic zone and the mixed layer are roughly identical in extent. Broecker and Peng (1974) have used the stagnant film model and radiocarbon and Radon data to evaluate air-sea gas exchange, and have estimated gas residence times (with respect to transfer to the atmosphere) in the mixed layer. They estimate that gases with normal molecular diffusivities—such as methyl halides—have a mean mixed-layer residence time of about 1 month for an 80 meter (North Pacific average) mixed layer depth. The exchange rate under these conditions is thus $4 \times 10^{-7}$ sec$^{-1}$. As the rate of methyl iodide hydrolysis in seawater is similar at 20°C and about one-third as large at 10°C, very substantial amounts of methyl chloride should by synthesized in seawater if the mechanism of Lovelock is correct. This methyl chloride has a long

<table>
<thead>
<tr>
<th>Halide</th>
<th>Nucleophile</th>
<th>$T^\circ C$</th>
<th>$K$'(sec$^{-1}$)*</th>
<th>Half-Life (yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$I</td>
<td>Saturated NaCl</td>
<td>19.2</td>
<td>$4.0 \times 10^{-6}$</td>
<td>0.0055</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10.8</td>
<td>$7.3 \times 10^{-7}$</td>
<td>0.030</td>
</tr>
<tr>
<td></td>
<td>19.0°/00</td>
<td>19.2</td>
<td>$3.5 \times 10^{-7}$</td>
<td>0.062</td>
</tr>
<tr>
<td>Chlorinity NaCl</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>19.8°/00</td>
<td>19.2</td>
<td>$4.1 \times 10^{-7}$</td>
<td>0.054</td>
<td></td>
</tr>
<tr>
<td>Chlorinity Sea Water</td>
<td>10.8**</td>
<td>$1.4 \times 10^{-7}$</td>
<td>0.16</td>
<td></td>
</tr>
<tr>
<td>Water (Calc.)</td>
<td>0</td>
<td>$9.4 \times 10^{-10}$</td>
<td>23</td>
<td></td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>$5.4 \times 10^{-9}$</td>
<td>4.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>$3.2 \times 10^{-8}$</td>
<td>0.69</td>
<td></td>
</tr>
<tr>
<td>CH$_3$Cl</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>$2.5 \times 10^{-10}$</td>
<td>88</td>
<td></td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>$1.6 \times 10^{-9}$</td>
<td>14</td>
<td></td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>$8.9 \times 10^{-9}$</td>
<td>2.5</td>
<td></td>
</tr>
</tbody>
</table>

* Pseudo first-order rate constant.  
** Over initial 42% of decay.
half-life for decomposition by known reactions in seawater (Table II), and it might represent a useful label for some surface-derived water masses. Methyl chloride should also exchange into the atmosphere, where (unlike methyl iodide) it will be photostable in the troposphere. The technique used by Lovelock et al., (1973) to detect methyl iodide is applicable with lesser sensitivity to methyl chloride.

Could reaction (1) be responsible for the well-known enrichment of sea-salt particles with I (Duce et al., 1965; Moyers and Duce, 1972; Seto and Duce, 1972; Martens, 1973) by way of evaporation of methyl iodide, dissolution in atmospheric salt droplets, and release of I? Using the rates for saturated salt solutions (Table 2), assuming that all gas-liquid exchange processes are fast, and conservatively taking the steady-state methyl iodide concentration dissolved in salt droplets to be the mean concentration found in surface water by Lovelock et al., (1973), the rate of I\textsuperscript{-} accumulation on a particle was estimated. About $7 \times 10^4$ reaction (1) half-lives are required for 100-fold enrichment of particle I/Cl over sea water I/Cl. This mechanism thus makes no contribution to I enrichment, as the marine aerosol has an atmospheric residence time of about one reaction (1) half-life (Junge, 1972).

Finally, experimental results agree with the qualitative reactivity order predicted by the Swain-Scott equation (Table I). Quantitatively, chloride reacts with methyl iodide about 11–26 times faster than water at 10–20°C, compared to the 9.4-fold estimate of Table I. Considering the approximations made, the agreement is satisfactory. The qualitative Swain-Scott reactivity order in seawater may be more generally applicable; since Swain-Scott $s$ values are always positive, the reactivity order of Table I should be followed for SN2 reactions on other substrates in sea water. The general reaction sequence will be conversion to chlorides, followed by slower hydrolysis to alcohols. Naturally occurring SN2-reactive compounds may be relatively rare, but many synthetic organic chemicals (phosphoric and sulfuric esters, alkyl halides, and some carboxylic esters) possess significant SN2 reactivity and are potential pollutants.

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REFERENCES


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