

## Photochemical production of methyl iodide in seawater

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**Abstract.** It is generally accepted that methyl iodide is a major contributor to the flux of iodine from the ocean to the atmosphere, but its sources in the ocean are largely unknown, an exception being production by certain species of coastal macrophytic algae. Preliminary results reported here indicate production of methyl iodide in filtered seawater that has been irradiated with either sunlight or an artificial light source having a spectral output closely approximating to sunlight at sea level. The production was enhanced when the water samples were deoxygenated and by the addition of iodide to this water. The results appear to be consistent with a mechanism involving reaction between photochemically produced methyl radicals and iodine atoms. It is estimated that the process is capable of making a significant contribution to global iodine fluxes.

### Introduction

The I/Cl ratio in rainwater exceeds that in seawater by a factor of  $\sim 300$  [Dean, 1963], and the source of this iodine is assumed to be the ocean which is the main reservoir of the element. A number of studies have looked at possible mechanisms for the transfer of iodine from the ocean to the atmosphere. Of these, several have focused on release of iodine from seawater on exposure to solar or ultraviolet radiation [Miyake and Tsunogai, 1963; Martens and Harriss, 1970] and reaction with ozone [Garland and Curtis, 1981]. Some difficulties exist in the interpretation of these experiments on account of the use of wavelengths outside the solar spectrum at sea level and because the radio-tracer techniques give little information on the chemical nature of the species involved in iodine transfer. It was suggested by Miyake and Tsunogai that photochemically produced molecular iodine is the carrier species for the ocean to atmosphere transfer. Such a mechanism is unlikely on account of the rapid rate of reaction of iodine in seawater, initially giving HOI [Eigen and Kustin, 1962] which finally reacts with organic matter [Truesdale, 1974, 1993; Truesdale and Moore, 1992]. An exception could occur if iodine is generated in the surface microlayer, for example by the reaction of ozone with iodide [Garland and Curtis, 1981]. Thompson and Zafriou [1983] have estimated that in this case molecular iodine could be generated rapidly enough to support atmospheric iodine levels.

More recently, work has tended to focus on organic iodine, particularly methyl iodide [Lovelock *et al.*, 1973; Lovelock, 1975; Singh *et al.*, 1983; Nightingale, 1991; Moore and Tokarczyk, 1993], chloriodomethane [Class and Ballschmiter, 1987; Klick and Abrahamsson, 1992; Moore and Tokarczyk, 1992], di-iodomethane [Class and Ballschmiter, 1988; Klick and Abrahamsson, 1992], and iodopropanes and butanes [Gschwend *et al.*, 1985; Klick and Abrahamsson, 1992]. The source of the volatile iodine compounds is

generally thought to be biological, with considerable evidence for marine macroalgal production [e.g., Gschwend *et al.*, 1985; Manley and Dastoor, 1987, 1988], but as yet, little for phytoplankton production. In the case of chloriodomethane there is evidence that it has, in part, a photochemical source from di-iodomethane [Class and Ballschmiter, 1988; Moore and Tokarczyk, 1993]. In this work a study has been made of the possible production of methyl iodide by the influence of sunlight on filtered seawater.

### Methods

Initial studies involved exposing filtered seawater in quartz vessels to sunlight. These were followed by more controlled laboratory experiments which employed a solar simulator (Oriel 300W). Water samples were filtered through 0.45- $\mu\text{m}$  silver filters to remove phytoplankton and then purged with ultra-high-purity helium or air to remove volatile halocarbons. In the experiments using natural sunlight, the irradiation was done in a 200-mL quartz vessel which served also as a purge vessel. Methyl iodide was analyzed by purging directly from the quartz vessel, trapping on Tenax, and desorbing into a gas chromatograph fitted with an electron capture detector (ECD) and a 30-m DB 624 column held at 35°C. This procedure was used before irradiation of the prepurged water to ensure that methyl iodide had been removed to blank levels of 0.4 pmol L<sup>-1</sup>. The system was calibrated by injecting a standard solution of methyl iodide in methanol, prepared by sequential dilution, into the purge vessel via a septum port. Irradiations were typically done beneath a clear sky, around noon (latitude 45°–53°N), for a period of about 1 hour.

Some improvements were made to these techniques in the subsequent controlled laboratory experiments. Water samples were filtered through 0.22- $\mu\text{m}$  membrane filters to remove phytoplankton and bacteria, and irradiations were done in a quartz cell fitted with a frit and holding 30 mL of water. The purge gas was dried by passage through a magnesium perchlorate tube, the volatiles trapped in an unpacked steel tube at  $-150^\circ\text{C}$ , and desorbed at  $100^\circ\text{C}$  into

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**Table 1.** Results of Initial Experiments Using Oxygenated Seawater and Natural Light

Light Conditions	Time, Hours	[CH <sub>3</sub> I] Light, pmol L <sup>-1</sup>	[CH <sub>3</sub> I] Dark, pmol L <sup>-1</sup>	Production Rate of CH <sub>3</sub> I, pmol L <sup>-1</sup> h <sup>-1</sup>
Sunlight	2.0	1.97		0.99
Sunlight	2.0	3.03		1.51
Overcast	0.9	0.14		0.16
Dark	15.5		1.90	0.12
Dark	2.0		0.56	0.28
Sunlight	1.0	9.37		9.37
Sunlight (+HA)	1.0	5.00		5.00
Dark (+HA)	1.3		0.56	0.43
Sunlight	1.7	1.27		0.75
Sunlight	1.7	2.04		1.20
Dark	19		0.92	0.05

Production rates for CH<sub>3</sub>I given in column 3 have not been corrected for dark production.

the gas chromatograph. Separation was achieved on a 30-m precolumn and 70-m main column (DB 624, 0.53-mm internal diameter). The system was calibrated by injection, via a septum port, of a methyl iodide solution in distilled water, prepared by sequential dilution of solutions in methanol. The purge efficiency ( $65 \pm 12\%$ ) of the quartz vessel was determined by making sequential measurements of a sample of seawater containing methyl iodide. A detection limit of  $\sim 0.02$  pM L<sup>-1</sup> of methyl iodide was achieved, and blanks of  $\sim 0.04$  pM L<sup>-1</sup>. The light source is designed to give a collimated light beam with a spectral distribution closely matching solar irradiation at sea level, at a solar zenith angle of 48°, and an intensity  $\sim 1325$  W m<sup>-2</sup> over the window 280–1100 nm [Oriel Corporation, 1993].

In each experiment a blank measurement was made of the increase in methyl iodide in the sample held in the dark for a period of time equal to that of the irradiation. This amount, due to contaminants and any dark production, was subtracted from the reported light production.

Gas chromatography–mass spectrometry (GC-MS) employed a Hewlett-Packard 5890 series II gas chromatograph fitted with a 30-m DB5 column (internal diameter 0.25 mm) coupled to a VG 20–150 quadrupole mass spectrometer. The instrument was set to scan the mass range 120–150 at 1 scan s<sup>-1</sup>.

## Results

Results of initial experiments using natural sunlight and oxygenated coastal North Sea water are summarized in Table 1. In sunlight there is a consistent production of methyl iodide which is well in excess of the blank measured in the dark samples. To one of the samples had been added a solution of terrestrial humic acid [Spokes, 1991] to a concentration of 5 mg L<sup>-1</sup> as a photosensitizer. This did not increase the production rate of methyl iodide.

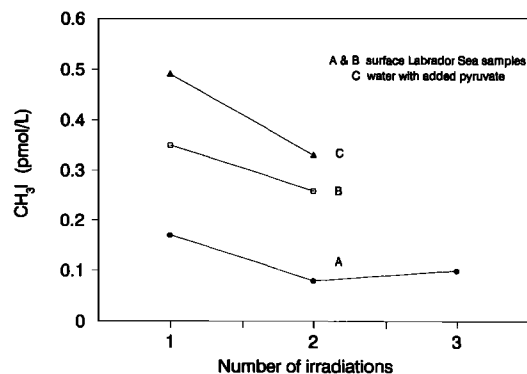
In view of the lack of control of radiation intensity, experiments of this kind were of limited value and were followed by a further set in which a solar simulator was used. Early experiments showed that methyl iodide production was substantially greater in seawater that had been purged with helium than in water purged with a nitrogen-oxygen (4:1) mixture. Since methyl iodide was more easily mea-

sured in experiments using nominally oxygen-free water, these conditions were selected for a series of measurements designed to provide clues as to the mechanism for methyl iodide production.

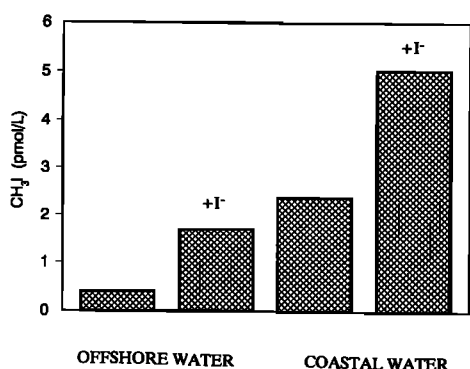
**Deoxygenated water.** The effect of sequential, short (4 min) irradiations of the same water sample was determined, and the results are shown in Figure 1. This figure includes a sample to which sodium pyruvate had been added at 11 μmol L<sup>-1</sup>; the reason for use of this compound is discussed below. A consistent tendency was observed for the rate of production of methyl iodide to decrease after the first irradiation; this could occur for a number of reasons. There could be a loss of the required chromophores or of the structural elements which are the source of the methyl group. Two possible explanations of the latter effect are, first, loss due to reaction of the organic matter and, second, loss of essential volatile constituents by purging. This last possibility can be excluded in the case where pyruvate appears to have been responsible for enhanced production of methyl iodide. The results of this experiment established the procedure to be used when examining the influence of various additions to water samples; namely, a fresh aliquot of water had to be used in each case.

**Influence of iodide concentration and origin of water sample.** Still using deoxygenated samples, a comparison was made of CH<sub>3</sub>I production in Labrador Sea water and coastal water. The two types were selected on account of the generally much higher concentration in coastal waters of light-absorbing organic compounds which are critical to making light energy available for reactions [Zika, 1981]. The coastal water is expected to differ not only in this respect but also, more generally, in dissolved organic matter content; this difference is likely to be significant in terms of the source of the carbon moiety of CH<sub>3</sub>I. Measurements of iodide in samples of the two water types showed substantially higher levels in the coastal (250 nM) than offshore (92 nM) water (A. Farrenkopf and G. Luther, personal communication, 1993).

As shown in Figure 2, the production rate of CH<sub>3</sub>I was about 6 times greater in the coastal water. When iodide was added to the Labrador seawater to a level of  $\sim 2.3$  μmol L<sup>-1</sup>, a fourfold increase in CH<sub>3</sub>I production occurred. To the



**Figure 1.** Effect of sequential 4-min irradiations on the same sample of oxygen-free water. Plotted is the concentration of CH<sub>3</sub>I in the sample at the end of each irradiation period. Lines A and B are surface Labrador Sea water and line C has added pyruvate.



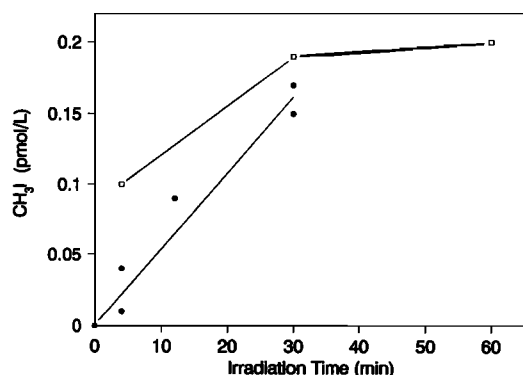
**Figure 2.** A comparison of methyl iodide production in an offshore (Labrador Sea) and coastal water sample, each with and without added iodide. All these samples are oxygen free.

coastal water sample was added a smaller quantity of I<sup>-</sup> (0.2 μmol L<sup>-1</sup>) which doubled the production rate.

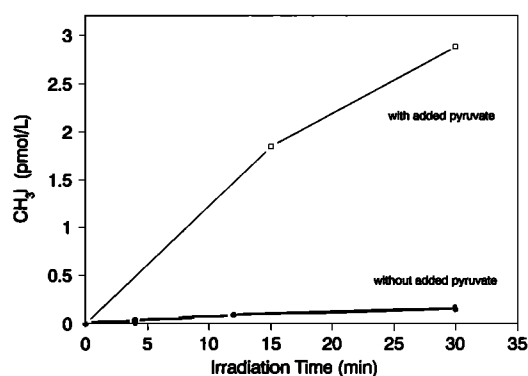
**Experiments with oxygenated water.** On account of very much lower rates of methyl iodide production in oxygenated waters than in deoxygenated samples it was found necessary to increase the irradiation time from 4 min to as long as an hour. Figure 3 shows the rate of production in oxygenated coastal seawater with no additions and with I<sup>-</sup> added to a level of 1.3 μmol L<sup>-1</sup>; this represents a fivefold increase in I<sup>-</sup> concentration. While in the case of the shortest irradiation times there appears to be a faster rate of production of methyl iodide, when the irradiation time was 30 min, the enhancement produced by the additional I<sup>-</sup> is small enough to be of questionable significance. The production rate tends to decrease as the irradiation time increases, but a rate of 0.2–0.3 pmol L<sup>-1</sup> h<sup>-1</sup> is a reasonable estimate.

As an initial attempt to assess free radical mechanisms for producing methyl iodide, sodium pyruvate was added to seawater samples as a simple, soluble, nonvolatile model organic substrate that photolyzes at significant rates at wavelengths in the solar spectral region and produces some of the transient species expected to play a role. At a concentration of 10.7 μmol L<sup>-1</sup> it provided an almost 20-fold increase in methyl iodide production (Figure 4).

Using the conditions that had been found to enhance



**Figure 3.** The effect of adding additional iodide (squares) to an oxygenated coastal seawater sample (circles). In these experiments the same aliquot of water is irradiated for several, increasing periods of time, and is totally purged of methyl iodide between successive irradiations.



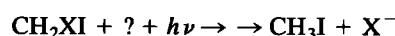
**Figure 4.** An illustration of the effect of adding sodium pyruvate to an oxygenated coastal water sample which is irradiated for varying periods. The samples are totally purged of methyl iodide between successive irradiations.

methyl iodide production, deoxygenation, iodide and pyruvate additions (1.8 and 11 μmol L<sup>-1</sup>, respectively), and a 10-min irradiation, a gas sample was trapped in a steel tube at -150°C for GC-MS measurement which confirmed the identity of the methyl iodide peak.

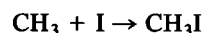
#### Discussion

The photochemical formation of methyl iodide poses a problem which the data here begin to address. The main plausible pathways would seem to be

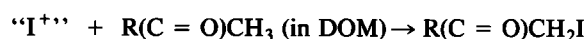
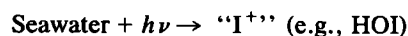
Path A: Reductive dehalogenation



Path B: Radical recombination



Path C: Photoiodoform reaction



Path A is without precedent to our knowledge and cannot explain the effect of added iodide, hence it is not considered further. Path C is expected to be favored by high pH and to result in postirradiation evolution of methyl iodide. Dark controls of the experiments described here were normally run after the irradiations and their results do not support significant continued evolution of methyl iodide. Hence it too is not considered further. Path B appears to be qualitatively consistent with the effects of adding iodide and oxygen (enhancement and inhibition, respectively). Its feasibility is considered more quantitatively below.

We require methyl iodide accumulation rates of ~1–10 pM L<sup>-1</sup> h<sup>-1</sup> (0.3–3 × 10<sup>-15</sup> mole CH<sub>3</sub>I L<sup>-1</sup> s<sup>-1</sup>) in oxygenated water and sunlight. Can radical fluxes support such a rate? A great variety of more temperate and tropical waters, including pelagic waters but excluding waters of low salinity have been shown to form free radicals (speciation largely unknown) at ~3–300 pM L<sup>-1</sup> s<sup>-1</sup> [Dister and Zafiriou, 1993], 4 to 6 orders of magnitude greater than rates required to sustain the observed methyl iodide production. Hence radi-

cal paths deserve detailed examination. Since exothermic radical-radical reactions generally proceed at nearly the diffusion-controlled rate in solution [Zafiriou *et al.*, 1990], we assume that the reaction  $\text{CH}_3 + \text{I}^- \rightarrow \text{CH}_3\text{I}$  is fast, and expect

$$+d[\text{CH}_3\text{I}]/dt \sim 5 \times 10^9 \times [\text{CH}_3][\text{I}] \text{ L mol}^{-1} \text{ s}^{-1} \quad (1)$$

Forming methyl iodide at  $0.3\text{--}3 \times 10^{-15} \text{ mol CH}_3\text{I L}^{-1} \text{ s}^{-1}$  via (1) then requires

$$[\text{CH}_3][\text{I}] = 0.06\text{--}0.6 \times 10^{-24} \text{ M}^2 \quad (2)$$

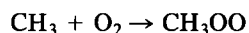
That is, for equal radical concentrations the steady state radical levels are 0.2–0.8 pM each. We consider the  $\text{CH}_3$  and I sources and sinks below.

Surface ocean waters contain  $\text{I}^-$  at 100–200 nmol  $\text{L}^{-1}$  [Jickells *et al.*, 1988; Luther *et al.*, 1988], and since this species is readily oxidized, many photochemical oxidants may provide a significant source of I atoms. These include OH radical [Mopper and Zhou, 1990] and its daughters,  $\text{Br}_2^-$  and  $\text{CO}_3^-$  [Zafiriou *et al.*, 1987], as well as alkylperoxy and acylperoxy radicals [Mill *et al.*, 1980; von Sonntag and Schucher, 1991]. Photolysis of all organic iodides also efficiently produces I atoms [e.g., Zika *et al.*, 1984]. Near the air-sea interface their formation may be promoted by ozone reactions [Waite *et al.*, 1988].

Sinks for I atoms are less clear. Although the abundant superoxide ion-radical [Micinski *et al.*, 1993] may rapidly reduce I to  $\text{I}^-$ , I atoms are otherwise rather unreactive. Hence high steady state concentrations seem quite plausible, especially where superoxide concentrations are kept low by superoxide dismutases or other sinks [Zafiriou, 1991].

The required methyl radicals are probably formed by photolysis of humic materials. Photolysis of humic materials in lake waters [Kieber and Blough, 1990] and in coastal seawater (N. V. Blough, personal communication, 1993) produces detectable fluxes of methyl and of acetyl ( $\text{CH}_3 - \text{C} = \text{O}$ ) radicals. Indeed, these are the most abundant specific organic radicals detected in such experiments, suggesting that their formation rates are more than adequate.

However, a major obstacle is posed by the large sink for methyl radicals through reaction with oxygen [Zafiriou *et al.*, 1990]:

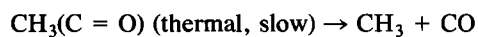


In air-saturated solution this reaction leads to a methyl radical half-life of only ~1 ms, requiring a  $1 \mu\text{mol L}^{-1} \text{ s}^{-1}$  formation rate to produce a steady state concentration of 1 pmol. Such a rate, if attainable, probably could not be sustained for long. Therefore in (2), [I] is likely to be much greater than  $[\text{CH}_3]$  if the radical mechanism for methyl iodide production is correct.

In summary the two major effects observed in manipulative experiments are easily explained by the radical mechanism. Enhanced production with increased  $[\text{I}^-]$  and with decreased  $[\text{O}_2]$  are rationalized naturally in terms of the expected major features of their cycles: an enhanced source of I and a diminished sink for  $\text{CH}_3$ , respectively. The enhanced I source arises because  $\text{I}^-$  competes with other reductants for oxidants, so the yield of I increases with increasing  $[\text{I}^-]$ .

The effect of added pyruvate is also highly suggestive of radical involvement in the broadest sense, since it decom-

poses photochemically by a radical mechanism [Closs and Miller, 1978] and is unlikely to have "direct" pathways in seawater medium. However, explaining its effects even qualitatively is difficult, since (1) it produces the strong reductant,  $\text{CO}_2^-$ , which might diminish [I] rather than increasing it; (2) the other major radical product, acetyl radical, has complex chemistry and is an inefficient source of  $\text{CH}_3$  via



under most conditions [Closs and Miller, 1978].

This difficulty is not severe enough to rule out the suggested radical path. For example, an alternative interpretation is that in the presence of trace  $\text{O}_2$ ,  $\text{CH}_3\text{CO}$  is converted via the "Russell mechanism" to  $2\text{CHCO}_2 + \text{O}_2$  [von Sonntag and Schucher, 1991]. Then  $\text{CH}_3\text{CO}_2$  radicals rapidly yield  $\text{CH}_3 + \text{CO}_2$  [Kraeutler and Bard, 1978]. Clearly, further experiments utilizing cleaner sources of ( $\text{I}^- + \text{oxidant}$ ), I alone,  $\text{CH}_3$  alone, and ( $\text{CH}_3 + \text{I}$ ) could evaluate the proposed pathway much more rigorously.

Turning to its geochemical role, we will estimate whether photochemical production of methyl iodide at the ocean surface has the potential to make a significant contribution to the total marine source of the compound, based on this limited data set. The global supply of methyl iodide from ocean to atmosphere was estimated by Liss and Slater [1974] to be  $2.7 \times 10^{11} \text{ g yr}^{-1}$ . This value was based on a concentration in seawater of 6 pmol  $\text{L}^{-1}$  and an exchange coefficient of 10.6  $\text{cm hr}^{-1}$ . As discussed by Nightingale [1991], this exchange coefficient is probably too high, and he used a value of 4  $\text{cm h}^{-1}$  for the North Sea, yielding an extrapolated global flux of  $1.4 \times 10^{11} \text{ g yr}^{-1}$  which he suggests is an upper limit on account of the high biological productivity of the areas in which his measurements were made. This lower flux is equivalent to a loss rate of 300 pmol  $\text{m}^{-2} \text{ h}^{-1}$ . Supporting such a flux would require production rates of 0.03, 0.3, and 3 pmol  $\text{L}^{-1} \text{ h}^{-1}$  in layers of water 10, 1, and 0.1 m thick, respectively.

From the measurements that have been made, there is no information on the wavelength dependence of the process which could be used to estimate how the production rate would decline through the euphotic zone. The greatest production rate found in the laboratory experiments for water samples to which no additions had been made was equivalent to 0.3 pmol  $\text{L}^{-1} \text{ h}^{-1}$ . Allowing for the light intensity in these experiments being approximately twice solar, photochemical production occurring at 0.15 pmol  $\text{L}^{-1} \text{ h}^{-1}$  over a 2-m layer would approximate to the escape rate (300 pmol  $\text{m}^{-2} \text{ h}^{-1}$ ) of methyl iodide from the ocean surface.

The earlier experiments in which coastal water samples were exposed to sunlight gave production rates typically of 0.7–1.4 pmol  $\text{L}^{-1} \text{ h}^{-1}$ . These results also support the idea that this process could be important in coastal waters. It should be noted that these experiments normally used lighting conditions equivalent to a clear sky and high Sun elevation. Furthermore, the calculated hourly fluxes of methyl iodide from ocean to atmosphere are for a 24-hour day, not just for hours of sunlight. These factors tend to exaggerate the importance of the photochemical process. Also, the production of methyl iodide in the oceans has to be larger than the escaping flux, on account of downward mixing, hydrolysis, and photochemical loss. It should be noted that photochemical decomposition of methyl iodide in

seawater is slow in comparison with the process described here, the minimum half-life in surface waters being ~5.5 days [Zika *et al.*, 1984].

It was not possible to determine whether the small increases in methyl iodide in the dark can be entirely accounted for by low levels of contamination or must contain an additional component arising from chemical processes in the sample. An example of such a process is the reaction described by White [1982] between dimethyl sulphonium propionate, a known algal metabolite [Challenger and Simpson, 1948], and iodide. While there is no evidence that the reaction occurs at a rate that is environmentally significant, it will presumably act as a finite source of methyl iodide. Additionally, while the experiments described here have been designed to reduce bacterial processes by filtering bacteria from the water samples, they are not entirely excluded and may conceivably provide an increasing influence as the duration of experiments increases.

In the oceans, direct biological production of methyl iodide by algae, macrophytic or unicellular, or by bacteria may well be important also, but the preliminary results presented here suggest that photochemical reactions can potentially play a significant role in the production as well as loss of methyl iodide in seawater.

## Conclusions

1. Preliminary experiments reported here indicate that methyl iodide is produced by the interaction of sunlight and seawater.

2. The presence of oxygen tends to inhibit the production, while addition of iodide enhanced it significantly in water samples that were deoxygenated.

3. Coastal water gave a higher production rate than offshore water, a result which could be due to its higher concentration of organic matter acting both as a light absorber and methyl radical source.

4. Generation of methyl iodide from photochemically produced methyl and iodine radicals appears to be a feasible pathway.

5. This process occurs at a rate which makes it potentially significant to the total production of methyl iodide in surface ocean waters and to the ocean supply of iodine to the atmosphere.

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