Adsorption and catalytic decomposition of methyl bromide and methyl iodide on activated carbons

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Abstract

Methyl bromide (MeBr) is commonly used for fumigating structures and commodities. Emission of MeBr during such treatments is environmentally detrimental because of the reaction of MeBr with stratospheric ozone. In this study we evaluated adsorption of MeBr and methyl iodide (MeI) – a potential MeBr replacement, on five commercial activated carbons, and studied water-initiated catalytic decomposition of adsorbed fumigants. All carbon samples showed great adsorption affinity to MeBr and MeI, with the adsorption capacity for MeI several times greater than that for MeBr on the same carbon. For the same fumigant, adsorption was affected by the type of carbon and the concentration of fumigant. Water initiated decomposition of both fumigants, liberating Br\textsuperscript{-} or I\textsuperscript{-} as a transformation product. The rate of decomposition increased with increasing temperature, and was also influenced by the carbon type. The half-life of MeBr or MeI on Centaur, a catalytically modified carbon, was < 2 h at 80\textdegree{}C. The rapid decomposition of MeBr and MeI on wet carbons at elevated temperatures may be used to detoxify these fumigants after adsorption on activated carbons. \copyright{} 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Methyl bromide; Methyl iodide; Methyl halides; Activated carbon; Adsorption; Fumigation; Fumigant; Catalytic decomposition; Emission control

1. Introduction

Methyl bromide (MeBr) is widely used as a fumigant for pest control in soil, commodity and structures (Honaganalli and Seiber, 1997). Studies have shown that 30–90\% of the applied MeBr in soil fumigation (Yates et al., 1997), and 80–95\% in commodity and structural fumigation (UNEP, 1995), is emitted into the atmosphere. Methyl bromide is highly reactive to ozone and is classified as a potent stratospheric ozone depletor. The use of MeBr will be discontinued by the year 2005 in the industrialized countries, with gradual reduction of use to occur after 2000. On the other hand, commodity and structural fumigation is essential for quarantine control in the international trade of agricultural and other products. However, few, if any, alternatives are available that may effectively replace MeBr in such uses (UNEP, 1995). It is clearly desirable to develop techniques for preventing MeBr emission, thus extending its use without inflicting any significant effects on the environment.

Unlike soil treatment, commodity and structural fumigation of MeBr is typically carried out in well-contained environment, such as chambers, rooms, storehouses, ships, and mills. The contained environment should facilitate recovery of MeBr at the end of treatment (UNEP, 1995). Activated carbons (AC) are known to absorb many inorganic and organic gases and are commonly used for the removal of these gases from waste water and air streams (e.g., Browne and Cohen, 1990; Ruhl, 1993; Hwang et al., 1997; Kim, 1997; Tanada et al., 1996). High carbon affinity was also reported for MeBr (Gan and Yates, 1998; Leesch et al., 2000) and MeI (Park et al., 1993). Modified or unmodified activated carbons may
also catalyze transformation of certain compounds in the adsorbed state, such as hydrogen sulfide (Turk et al., 1989; Dalai et al., 1999) and sulfur dioxide (Zhao et al., 1994). However, catalytic decomposition by activated carbon has not been reported for MeBr.

In this study adsorption isotherms of gaseous MeBr and MeI were obtained for five commercial carbons with varied properties. Catalytic decomposition of these fumigants was subsequently determined after addition of water and equilibration at different temperatures. Methyl iodide (MeI) was considered because it is structurally analogous to MeBr and is being developed as an alternative to MeBr (Gan and Yates, 1996; Becker et al., 1998; Hutchinson et al., 1999). Although not an ozone depletor, MeI is acutely toxic and potentially carcinogenic (The Merck Index, 1996) and therefore control of its emission will be necessary. The information from this study may be used for developing methods to decontaminate MeBr- or MeI-containing gases before their release to the atmosphere.

2. Materials and methods

2.1. Activated carbons and chemicals

Five granular activated carbons (12 × 20 mesh) were obtained from Calgon Co. (Pittsburgh, PA) and used in this study. The basic characteristics of these carbons are given in Table 1. These carbons were selected because of their differences in catalytic capacity. Among these samples, Centaur and Centaur-A are catalytically enhanced, bituminous coal-based carbons, BPL-F3 and F-820 are unmodified bituminous coal-based carbons, and GRC is a coconut shell-derived carbon.

Liquid MeBr was obtained from TriCal Co. (Hollister, CA), and MeI from Aldrich (Milwaukee, WI). Both chemicals had a purity > 99%. Before use, MeBr was introduced into a Teflon gas-sampling bag and the gaseous MeBr had a vapor density of 3.7 mg ml⁻¹ at 20°C.

2.2. Adsorption experiment

Adsorption of MeBr and MeI on the five carbons was determined in a batch adsorption experiment. Two grams of activated carbon were placed in 21-ml glass headspace vials, and the vials were capped with Teflon-faced butyl rubber septa and aluminum crimp seals. Various amounts of gaseous MeBr (0.25–32 ml) or liquid MeI (0.5–64 μl) were injected into the closed vials using gas-tight syringes. The actual quantity of MeBr or MeI added in each container was determined by weighing the difference to 0.1 mg before and after the spiking. After equilibration at 20°C for > 24 h, 0.5 ml of the headspace was drawn from each vial using a gas-tight syringe and injected into a Hewlett-Packard HP6890 gas chromatograph (GC) for analysis. An electron capture detector was used for detection, and the GC column was Rtx-624 (30 m × 0.32 mm × 1.4 μm, Restek, Bellefonte, PA). The column flow rate was 1.2 ml min⁻¹ (helium) and the split ratio was 50 : 1. The inlet and detector temperatures were 220 and 300°C, respectively, and the oven was held isothermally at 40°C. Fumigant concentration in the gas phase was obtained from the GC analysis, and adsorbed concentration on carbon was calculated from the difference between the spiked amount and fumigant distribution in the headspace.

Adsorption isotherms of MeBr and MeI on the five carbons were constructed by fitting the adsorbed and headspace concentrations to the Freundlich equation

\[
C_e = K_f C_w^n,
\]

where \( C_e \) (mg g⁻¹) is adsorbed fumigant concentration on carbon, \( C_w \) (mg l⁻¹) the concentration in the headspace, \( K_f \) the Freundlich adsorption coefficient (g l⁻¹), and \( n_f \) the slope of the linearized isotherm. Adsorption

<table>
<thead>
<tr>
<th>Carbon</th>
<th>Apparent density (g cm⁻³)</th>
<th>Ash (%)</th>
<th>Butane activity (g 100 g⁻¹)</th>
<th>Iodine number (mg g⁻¹)</th>
<th>Moisture (%)</th>
<th>Peroxide number (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Centaur-A</td>
<td>0.514</td>
<td>6.3</td>
<td>26.0</td>
<td>1101</td>
<td>2.8</td>
<td>4.2</td>
</tr>
<tr>
<td>BPL-F3</td>
<td>0.376</td>
<td>9.7</td>
<td>33.5</td>
<td>1154</td>
<td>5.4</td>
<td>24.0</td>
</tr>
<tr>
<td>GRC-22</td>
<td>0.466</td>
<td>1.3</td>
<td>27.0</td>
<td>1247</td>
<td>4.6</td>
<td>510.7</td>
</tr>
<tr>
<td>F820</td>
<td>0.537</td>
<td>5.5</td>
<td>20.8</td>
<td>951</td>
<td>5.0</td>
<td>43.0</td>
</tr>
<tr>
<td>Centaur</td>
<td>0.590</td>
<td>4.0</td>
<td>17.9</td>
<td>836</td>
<td>5.0</td>
<td>10.9</td>
</tr>
</tbody>
</table>

*Pore volume.

*Surface area.

*Catalytic activity.

*Extrapolated from measured values.
isotherms from different treatments were statistically evaluated by performing t-test for $K_t$ or $n_t$.

2.3. Degradation experiments

Water-initiated catalytic decomposition of MeBr and MeI on activated carbons was determined at 20, 50 and 80°C, in which both the disappearance of MeBr or MeI and the accumulation of Br$^-$ or I$^-$ were simultaneously determined. Preparation of MeBr- or MeI-laden carbons was carried out in sealed 21-mL headspace vials containing 2.0 g of activated carbon. To add MeBr, 20 mL of gaseous MeBr was injected into the closed vials using a syringe, and the actual amount measured by weighing. The average amount of MeBr added onto the 2.0 g carbon was 72 mg. To add MeI, 10 mL of liquid MeI was injected into the closed vials and the average amount added was measured to be 22 mg. The treated vials were kept in a freezer (−21°C) overnight. To initiate fumigant decomposition, the sample vials were opened while still cold and 1.0 mL of deionized water was added. The vials were immediately capped again with new septa and seals. The moist carbon samples were equilibrated at 20, 50, or 80°C. At 1, 3, 8, 24, 48 and 96 h after equilibration, 3 replicate samples from each carbon-temperature combination were removed and immediately transferred to a freezer (−21°C). To extract residual fumigant from carbons, sample vials were decapped and 4.0 mL of acetone and 5 g of anhydrous sodium sulfate were added, followed by immediate recapping. The capped vials were vigorously vortexed for 2.0 min, and after the carbon granules had settled, a fraction of the acetone extract was transferred to a GC vial. Quantification of fumigant concentration was made by injecting 2 μL liquid into the GC using analytical conditions given above.

Disappearance of fumigants with time was fitted to a first-order decay model

$$C = C_0 e^{-kt},$$

where $C$ (mg g$^{-1}$) is the overall fumigant concentration remaining in the vial at time $t$ (h), $C_0$ (mg g$^{-1}$) the initial added concentration, and $k$ the first-order degradation rate constant (h$^{-1}$). Degradation curves from different treatments were statistically evaluated by performing t-test for $k$.

At the same sampling intervals, triplicate samples were also taken for analysis of Br$^-$ (MeBr samples) or I$^-$ (MeI samples). Carbon granules in each vial were washed into a container with 20 mL of water and vigorously vortexed for 2.0 min, and the water solution was decanted into a collection flask. This extraction step was repeated for two more times, and water extracts were combined for the same sample. An aliquot of the extract was transferred to an ion chromatography (IC) vial for quantification on a Dionex-100 IC analyzer. An AS-14 column (Dionex, Sunnyvale, CA) was used for separation, and a mixture of 3.5 mM Na$_2$CO$_3$ and 1.0 mM NaHCO$_3$ was used as the mobile phase. The flow rate of the mobile phase was kept at 1.2 mL min$^{-1}$.

3. Results and discussion

3.1. Adsorption on activated carbons

For the concentration ranges used in this experiment, a good fit to the Freundlich equation was found for all the test carbons, as shown in Fig. 1a for MeBr treatments and Fig. 1b for MeI treatments. Overall, as indicated by the $K_t$ values in Table 2, the coconut-based GRC carbon showed the greatest adsorption for both MeBr and MeI, while the other four carbons were comparable in adsorbing these two fumigants (Table 2). However, the value of $n_t$ was consistently smaller than 1.0, suggesting that as the concentration of MeBr or MeI increased, the relative adsorption of fumigant decreased. For the adsorption of either MeBr or MeI, the relative order of $n_t$ was
Table 2
Freundlich coefficients $K_f$ (l g$^{-1}$) and $n_f$ for adsorption of methyl bromide and methyl iodide on activated carbons at 20°C

<table>
<thead>
<tr>
<th>Carbon</th>
<th>Methyl bromide</th>
<th>Methyl iodide</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$K_f$</td>
<td>$n_f$</td>
</tr>
<tr>
<td>Centaur-A</td>
<td>24.2</td>
<td>0.53</td>
</tr>
<tr>
<td>BPL-F3</td>
<td>16.4</td>
<td>0.67</td>
</tr>
<tr>
<td>GRC-22</td>
<td>34.2</td>
<td>0.80</td>
</tr>
<tr>
<td>F820</td>
<td>21.8</td>
<td>0.59</td>
</tr>
<tr>
<td>Centaur</td>
<td>22.8</td>
<td>0.50</td>
</tr>
</tbody>
</table>

GRC > BPL-F3 > F820 > Centaur-A $\approx$ Centaur, and the difference was significant at $P = 0.01$. This order determined that at the low end of the concentration range, adsorption was greater on the Centaur carbons than on the other carbons, while at the high concentrations, adsorption on the GRC carbon was the greatest (Fig. 1). For MeBr, adsorption on Centaur-A and Centaur carbons was greater than the other carbons when the adsorbed concentration was $< 3.5$ mg g$^{-1}$, but adsorption on GRC surpassed the other carbons when the adsorbed concentration was $> 14$ mg g$^{-1}$ (Fig. 1a). For MeI, adsorption on the Centaur carbons was the greatest when the adsorbed concentration was $< 5$ mg g$^{-1}$, but GRC adsorbed more fumigant when the concentration was $> 18$ mg g$^{-1}$ (Fig. 1b). These results imply that different carbons should be used for removing fumigants of different concentrations. Of the selected carbons, Centaur carbons would be more effective for removing low concentrations of MeBr or MeI, while the GRC carbon would be more efficient for removing these compounds at sufficiently high concentrations. The $K_f$ values were regressed against the properties of carbon from Table 1. No significant correlation was found between fumigant adsorption and any single properties of carbon.

On the same carbon, MeI was consistently adsorbed to a much greater extent than MeBr (Table 2). Overall, $K_f$ for MeI adsorption was 3.5–6.0 times greater than that for MeBr adsorption on the same carbons. The slope of the isotherms, as measured by $n_f$, was similar between the two fumigants. The greater adsorption affinity of carbons to MeI may be attributed to the relatively lower vapor pressure of MeI (398 mmHg at 20°C) than that of MeBr (1600 mmHg at 20°C). This implies that the same amount of carbon may be used to remove a greater amount of MeI than MeBr.

3.2. Decomposition of MeBr and MeI on wet carbons

Decomposition of MeBr and MeI on carbons after addition of water was measured at 20, 50 and 80°C, and the measurement was fitted to a first-order decay model. As shown in Fig. 2 for MeBr and in Fig. 3 for MeI, a good fit was found for all the treatments, with the correlation coefficient $R$ ranging 0.78–1.00. The rate of fumigant decomposition increased as the equilibration temperature increased, and was also somewhat dependent on the carbon type (Figs. 2 and 3; Tables 3 and 4). Fumigant decomposition at the ambient temperature (20°C) was noticeable, but relatively slow. The estimated first-order half-life ($t_{1/2}$) was 100–385 h for MeBr and 95–365 h for MeI (Tables 3 and 4). These rates imply that although fumigant decomposition could occur at ambient temperature, it may take weeks or months to achieve complete decomposition ($\geq 99$% dissipation). When the
temperature increased to 50°C, fumigant decomposition was substantially enhanced. For MeBr, \( t_{1/2} \) was reduced by 4.6–10 times from the 20°C treatments, with \( t_{1/2} \) ranging from 22 to 39 h. With these \( t_{1/2} \) values, complete decomposition may be obtained within one week. For MeI, except for the coconut-based GRC carbon, \( t_{1/2} \) ranged from 9 to 20 h. Therefore, except for GRC, a few days to one week would be adequate to achieve complete decomposition of MeI at 50°C. When the temperature further increased to 80°C, fumigant decomposition became extremely rapid (Tables 3 and 4). For MeBr, \( t_{1/2} \) decreased to only 1.6–3.4 h, while for MeI, \( t_{1/2} \) decreased to only 1.0–3.8 h. With such decomposition rates, complete fumigant destruction may be achieved overnight.

At the same temperature, fumigant decomposition occurred at different rates when adsorbed on different carbons. At all temperatures, the most rapid decomposition consistently occurred on Centaur for both MeBr and MeI, with \( t_{1/2} \leq 2 \) h at 80°C (Tables 3 and 4). The slowest decomposition of both fumigants was found with the coconut-based GRC carbon in most treatments. Fumigant decomposition was comparable among the two coal-based carbons BPL-F3 and F820. Decomposition of MeI was significantly faster on Centaur-A at 50 and 80°C than the other carbons (Table 4). The dependence of fumigant decomposition rate on carbon type only generally agrees with the catalytic capacity of carbons as indicated by their peroxide numbers (Table 1). Regression analysis did not reveal a significant linear relationship. This may have been caused by the inclusion of the very high peroxide number of GRC that was obtained after extrapolation (Table 1). Other carbon characteristics such as apparent density, pore volume, and surface area may have also contributed in conjunction with catalytic activity to the differences among the activated carbons. Except on the coconut-based GRC, where comparable decomposition rate was observed between MeBr and MeI, decomposition of MeI was generally more rapid than MeBr at 50 and 80°C (Tables 3 and 4).

---

### Table 3

<table>
<thead>
<tr>
<th>Carbon</th>
<th>20°C</th>
<th>50°C</th>
<th>80°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( k )</td>
<td>( R )</td>
<td>( k )</td>
</tr>
<tr>
<td>Centaur-A</td>
<td>0.0030</td>
<td>0.95</td>
<td>0.0182</td>
</tr>
<tr>
<td>BPL-F3</td>
<td>0.0021</td>
<td>0.95</td>
<td>0.0193</td>
</tr>
<tr>
<td>GRC-22</td>
<td>0.0018</td>
<td>0.93</td>
<td>0.0176</td>
</tr>
<tr>
<td>F820</td>
<td>0.0033</td>
<td>0.99</td>
<td>0.0181</td>
</tr>
<tr>
<td>Centaur</td>
<td>0.0069</td>
<td>0.95</td>
<td>0.0318</td>
</tr>
</tbody>
</table>

---

### Table 4

<table>
<thead>
<tr>
<th>Carbon</th>
<th>20°C</th>
<th>50°C</th>
<th>80°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( k )</td>
<td>( R )</td>
<td>( k )</td>
</tr>
<tr>
<td>Centaur-A</td>
<td>0.0035</td>
<td>0.98</td>
<td>0.0791</td>
</tr>
<tr>
<td>BPL-F3</td>
<td>0.0019</td>
<td>0.78</td>
<td>0.0418</td>
</tr>
<tr>
<td>GRC-22</td>
<td>0.0051</td>
<td>0.88</td>
<td>0.0114</td>
</tr>
<tr>
<td>F820</td>
<td>0.0025</td>
<td>0.87</td>
<td>0.0356</td>
</tr>
<tr>
<td>Centaur</td>
<td>0.0073</td>
<td>0.99</td>
<td>0.0669</td>
</tr>
</tbody>
</table>

---

**Fig. 3.** Disappearance of methyl iodide on wet carbons at different temperatures.
This may be attributed to the fact that the strength of C–I bond in MeI (234 kJ mol⁻¹) was smaller than that of C–Br bond in MeBr (293 kJ mol⁻¹) and therefore easier to be broken (McMurry, 1992).

As MeBr and MeI dissipated in the acetone extract, Br⁻ and I⁻ were recovered in the water extract of the carbon samples. The accumulation of Br⁻ from carbons spiked with MeBr is shown in Fig. 4. As the equilibration time increased, the recovery of Br⁻ as the fraction of spiked MeBr consistently increased. However, it is apparent that Br⁻ only accounted for a part of the observed MeBr loss. For instance, although complete MeBr decomposition occurred after 24 h of equilibration at 80°C, the recovery as Br⁻ was < 63%. Similar recoveries were also found for I⁻ from samples treated with MeI. This suggests that the halide liberated during fumigant decomposition was only partially extractable using water as the solvent. The incomplete recovery of Br⁻ and I⁻ was confirmed when more halide ions were detected following additional extractions. In a study where an activated carbon biofilter was used to remove trichloroethylene (TCE) and tetrachloroethylene (PCE), only fractions (22–57%) of the removed TCE and PCE was observed as Cl⁻ in the aqueous effluent (Kim, 1997). Nevertheless, the fact that a large fraction of the decomposed MeBr or MeI was recovered as halide ions in this study suggests that catalysis by carbon resulted in extensive cleavage of the C–Br or C–I bond.

Cleavage of carbon–halogen bonds on carbons was previously reported only for temperatures ≥ 300°C (Burdeniuc and Crabtree, 1996; Tanada et al., 1996; Nicoll and Francisco, 1999). This study showed that methyl halides such as MeBr and MeI were catalytically decomposed by carbon in the presence of water at relatively low temperatures. The rapid decomposition of MeBr and MeI on moistened carbons can potentially be used to detoxify fumigants after adsorption on activated carbons. Since only water and relatively low temperature (< 100°C) are required, applications of this detoxification procedure may be easily engineered. After decomposition, the carbon may be rinsed off the transformation product Br⁻ or I⁻, and the carbon may be used again after drying and activation. The treatment should be rapid, cost-effective and safe, and therefore suitable for on-site application, eliminating the need to transport toxic carbons to off-site facilities for disposal.

4. Conclusions

All of the five activated carbons used for this study showed high adsorption affinity to gaseous MeBr and MeI. Fumigant adsorption was apparently dependent on the carbon type, as well as on the fumigant concentration. The Centaur carbons adsorbed more MeBr and MeI at low concentrations, while the coconut-based GRC carbon adsorbed more fumigants at high concentrations. Adsorption of MeI was several times greater than that of MeBr for the same carbons. Decomposition of MeBr and MeI adsorbed on carbons occurred upon addition of water, and the rate of decomposition increased with increasing temperature. At 80°C, the decomposition of both MeBr and MeI was so rapid on all the tested carbons that complete fumigant destruction was achieved in < 24 h. Under the same conditions,
decomposition of MeBr and MeI was more rapid on catalytically enhanced carbons than on non-catalytic carbons. These findings together suggest that activated carbons may be used to adsorb MeBr or MeI in fumigation effluents, and that the fumigant-contaminated carbon may be rapidly detoxified simply by adding water and heating the moistened carbon.

Acknowledgements

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References


