溴代烷烃光氧化的研究*

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摘要　本文模拟大气条件，研究了 $CH_3Br+H_2O_2+O_2$，CH_3Br+O_2，$CHBr_3+H_2O_2+O_2$，和 $CHBr_3+O_2$ 4个体系的光化学反应。这些体系在253.7 nm的紫外光照射下 H_2O_2 产生了OH自由基，OH自由基与 CH_3Br 和 $CHBr_3$ 反应，在20 m的长光程气体池中用FTIR测量这些反应产物，发现在 $CH_3Br+H_2O_2+O_2$ 和 CH_3Br+O_2 体系其光化学反应产物为CO，CO_2，CH_2O 和 H_2O，对 $CHBr_3+H_2O_2+O_2$ 其光化学反应产物为CO，CO_2 和 H_2O，对 $CHBr_3+O_2$ 其光化学反应产物为CO和 CO_2，并从这些产物推出可能发生的光化学反应。

关键词　光氧化反应，OH自由基，溴代烷烃。

已证实溴化物可对臭氧层造成破坏[1]。人们已经认识到R—Br键比R—Cl键不仅有更大的吸收截面，而且有更长的吸收波长，尽管它在大气中的浓度要比氯原子低，但每个溴原子破坏臭氧的能力要比氯原子大100倍[2—6]，所以它更容易参与破坏臭氧的循环反应。模拟对流层的条件，研究溴代烷烃与OH自由基或氧在紫外线的辐照下发生的反应及产物。研究溴甲烷和溴仿在大气中可能发生的光化学反应及其产物，对控制溴代烷烃的传输有重要意义。目前这类研究甚少。笔者通过富里叶红外光谱仪测量光化学反应的产物，从产物推出可能发生的反应机理。

1　实验部分

1.1　化学试剂

CH_3Br：分析纯，纯度＞98%（江苏激素所生产）；$CHBr_3$：分析纯，纯度＞98%（北京通县化工厂生产）；H_2O_2：分析纯，浓度30%（天津东方化工厂生产）；氧气：纯度＞99.9%（北京气体厂生产）。

1.2　气体配制

气体配制见图1。首先将系统抽控到13 Pa，用微量注射器将样品通过硅胶垫注入系统中配成所需要的样。

1.3　FTIR测定光化学反应产物

光照实验设备参看文献[7]，辐照时间1 h。将20 m长的长光程池抽空到13 Pa以下，然后把辐照后的样品移入其中，用Nicolet60 Sαβ富里叶红外光谱仪测定光解产物。检测器（MCT-B型）波数范围6000—400 cm^{-1}，分辨率2 cm^{-1}，每次记录的图谱是64扫描累加而成。

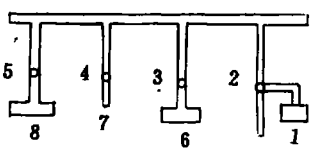

图1　配气装置

1. 真空泵　2、3、4、5 真空阀　6. 毫巴表　7. 硅胶垫　8. 光照池

2　结果和讨论

2.1　$CH_3Br+H_2O_2+O_2$ 体系

图2是30 μl CH_3Br+50 μl H_2O_2+20 μl O_2 光照1 h用FTIR测的红外光谱，图3是图2的红外光谱减去未经光照的相同体系的红外光谱图。从图3可以看出，1720—1760 cm^{-1}，2800—2900 cm^{-1} 是 CH_2O 的吸收峰，1400—1800 cm^{-1}、3600—3800 cm^{-1} 锯齿形峰是 H_2O，2300—2390 cm^{-1}，1343和667 cm^{-1} 是 CO_2 峰，2080—2150 cm^{-1}，2150—2220 cm^{-1} 是CO吸收峰，此体系经光照后生成 CH_2O，H_2O，CO_2 和CO，这些产物可能有如下的反应发生：

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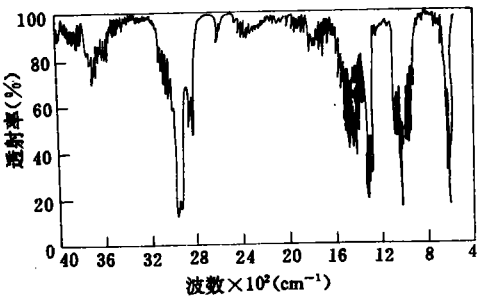

图 2　$CH_3Br+H_2O_2+O_2$ 光照 1 h 红外光谱

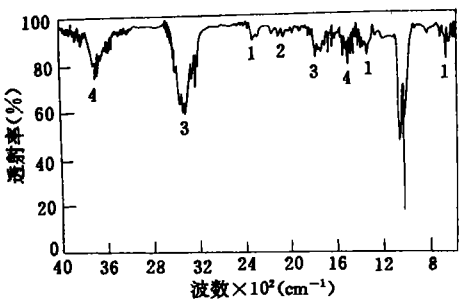

图 3　$CH_3Br+H_2O_2+O_2$ 光照 1 h 产物的红外光谱
1. CO_2　2. CO　3. CH_2O　4. H_2O

$$H_2O_2 \xrightarrow{h\nu} 2OH$$
$$CH_3Br+OH \longrightarrow CH_2Br+H_2O$$
$$CH_2Br+O_2 \longrightarrow CH_2BrO_2$$
$$2CH_2BrO_2 \longrightarrow 2CH_2BrO+O_2$$
$$CH_2BrO+OH \begin{cases} \longrightarrow CH_2O+HOBr \\ \longrightarrow H_2O+CHBrO \end{cases}$$
$$CHBrO \longrightarrow CO+HBr$$
$$2CO+O_2 \longrightarrow 2CO_2$$

2.2　CH_3Br+O_2 体系

图 4 是 30 μl CH_3Br + 20 μl O_2 光照 1 h 用 FTIR 测的红外光谱，图 5 是图 4 的红外光谱减去未经光照的相同体系的红外光谱图。

经光化学反应后生成的化合物有 CO_2，CO，CH_2O 和 H_2O。从这些产物的分析，可能有如下的反应发生：

$$CH_3Br \xrightarrow{h\nu} CH_3+Br$$
$$CH_3+O_2 \longrightarrow CH_3O_2 \longrightarrow CH_2O+OH$$
$$Br+OH \longrightarrow HOBr$$
$$CH_3Br+OH \longrightarrow CH_2Br+H_2O$$
$$CH_2Br+O_2 \longrightarrow CH_2BrO_2$$
$$2CH_2BrO_2 \longrightarrow 2CH_2BrO+O_2$$
$$2CH_2BrO \longrightarrow 2CH_2O+Br_2$$
$$CH_2BrO+O_2 \longrightarrow HO_2+CHBrO$$
$$CHBrO \longrightarrow CO+HBr$$
$$2CO+O_2 \longrightarrow 2CO_2$$

2.3　$CHBr_3+H_2O_2+O_2$ 体系

图 6 是 30 μl $CHBr_3$ + 50 μl H_2O_2 + 20 μl O_2 光照 1 h 测的 FTIR 红外光谱图。

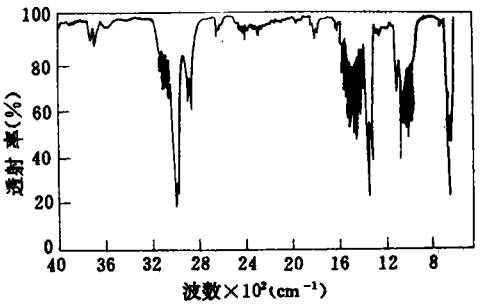

图 4　CH_3Br+O_2 光照 1 h 红外光谱

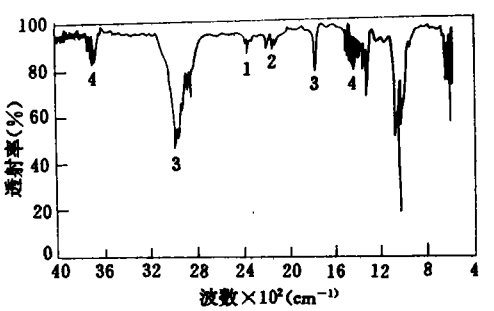

图 5　CH_3Br+O_2 光照 1 h 产物的红外光谱
1. CO_2　2. CO　3. CH_2O　4. H_2O

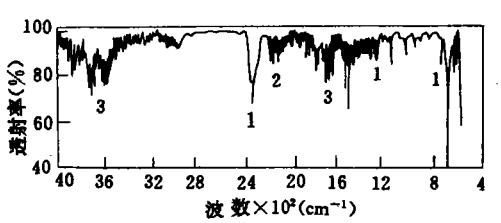

图 6　$CHBr_3+H_2O_2+O_2$ 光照 1 h 红外光谱

CO_2，CO 和 H_2O 为此体系的光化学反应产物，可能发生的光化学反应为：

$$H_2O_2 \xrightarrow{h\nu} 2OH$$
$$CHBr_3+OH \longrightarrow CBr_3+H_2O$$
$$CBr_3+O_2 \longrightarrow CBr_3O_2$$
$$2CBr_3O_2 \longrightarrow 2CBr_3O+O_2$$
$$CBr_3O+OH \longrightarrow CBr_2O+HOBr$$

$CBr_2O+OH \longrightarrow CBr_2OOH$

$\longrightarrow CBrO+HOBr$

$CBrO+OH \longrightarrow CBrOOH$

$CBrOOH \longrightarrow CO_2+HBr$

反应中仅需2个OH自由基和1个氧就能生成CBr_2O. 多余的OH自由基能将CBr_2O氧化完，所以产物中未检出CBr_2O。

2.2 $CHBr_3+O_2$ 体系

图7为30μl $CHBr_3$+20 μl O_2 光照1 h红外光谱图。此体系的光化学反应产物为CO_2和CO，可能发生的光化学反应为：

$CHBr_3 \xrightarrow{h\nu} CHBr_2+Br$

$CHBr_2+O_2 \longrightarrow CHBr_2O_2$

$2CHBr_2O_2 \longrightarrow 2CHBr_2O+O_2$

$CHBrO \longrightarrow CO+HBr$

$2CO+O_2 \longrightarrow 2CO_2$

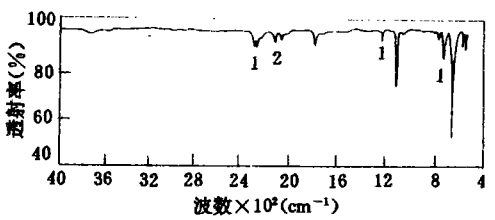

图7　$CHBr_3+O_2$ 光照1 h红外光谱

1. CO_2　2. CO

表1列出了CH_3Br和$CHBr_3$光解氧化或由OH自由基引发氧化4个反应体系生成的主要产物及其产率。从表1可以看出，CH_3Br与OH自由基反应或与O_2反应，其主要产物都为CO、CO_2和CH_2O，$CHBr_3$与OH自由基或与O_2起反应，其产物为CO、CO_2。从产物的产率分析，由OH自由基引发氧化溴代烷烃比溴代烷烃光解再与氧的反应要快，这可从键的解离能说明。HO—OH键解离能为2.15 eV/mol，C—Br键解离能为2.97 eV/mol。所以这些反应物在光照条件下，首先是H_2O_2解离成2个OH自由基，而活泼的OH自由基与溴代烷烃发生抽取氢的反应。根据文献[10]，其速率常数在298 K时$K=(3.03\pm0.45)\times10^{-14}cm^3mol^{-1}s^{-1}$，是一个很快的反应，所以在有$H_2O_2$存在时，溴代烷烃的光氧化是与OH自由基反应。$CH_3Br+H_2O_2+O_2$和$CHBr_3+H_2O_2+O_2$体系总的变化率分别为26.7%和50%。但在没有$H_2O_2$存在时，光照首先使溴代烷中C—Br键断裂，生成$CH_3\cdot$或$CHBr_2\cdot$和Br·基，而这些自由基再与$O_2$反应，从反应产率分析，对$CH_3Br+O_2$和$CHBr_3+O_2$体系总的变化率分别为15.7%和21%。对同类的溴代烷烃在有过氧化氢存在或有氧存在下的光解其变化率有差别，前者快1倍多。

从4个体系推出可能发生的反应，产物中应有HBr，但在2649 cm^{-1}处没有出现吸收峰，可能是HOBr和HBr反应生成Br_2和H_2O，所以未检出HBr。而Br_2在红外没有吸收峰，但从本实验的光解池可明显看出有红棕的Br_2。

表1　光照1h 4个体系主要产物及其产率(%)

体　系	CO	CO_2	CH_2O	总变化
$CH_3Br+H_2O_2+O_2$	4.5	8.2	14	26.7
CH_3Br+O_2	3.1	3.1	9.5	15.7
$CHBr_3+H_2O_2+O_2$	16.7	33.3		50
$CHBr_3+O_2$	14	7		21

3　结论

(1) CH_3Br光解氧化或与OH自由基光化学反应其产物为CO，CO_2，CH_2O和H_2O。

(2) $CHBr_3$与OH自由基光化学反应，有氧存在时其反应产物为CO_2、CO和H_2O，$CHBr_3$光解与氧反应，其产物为CO_2和CO。

(3) 大气中的溴代烷烃与OH自由基通过光氧化反应的速度比其光解与氧反应速度快。

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Abstracts

Chinese Journal of Environmental Science

Microbial Purification and Recovery of Pu-239 from Nuclear Industrial Wastewater. Li Fude et al. (Chengdu Institute of Biology, Chinese Academy of Sciences, Chengdu 610041): *Chin. J. Environ. Sci.*, **16**(6), 1995, pp. 1—3

From Pu-containing wastewater from nuclear industry, 13 strains of bacteria were isolated and screened out, and observed for their abilities of enriching Pu-239. One of them, called strain OR, was found to be one which can efficiently accumulate Pu-239 and to have the highest capacity of accumulating Pu-239 as compared to *Desulphovibrio* sp., *S. cerevisiae*, *Actionmycetes* sp., and *Rhizopus* sp.. The optimum conditions under which strain OR can efficiently accumulate Pu-239 were pH6, 30°C, and a dosage of 0.05 g wet culture per ml of solution to be treated. Under these conditions, a Pu-239 removal of 99% was given by reacting for 5 min. and up to 97% of Pu-239 were recovered by desorbbing 2 times with 0.5 mol/L of $NaHCO_3$. Alpha-energy spectrometric detection showed the presence of Pu-239 in the cells of strain OR. The analysis using scan electronic microscope in combination with transmission electronic microscope showed that the adsorption of Pu-239 onto strain OR occurred mainly due to the surface adsorption and flocculation of cell walls.

Key words: microbe, Pu-239, purification, recovery.

Study on the Photooxidation of Brominated Alkanes. Zhong Jinxian et al. (Research Center for Eco-Environmental Sceinces, Chinese Academy of Sciences, Beijing 100085), Chen Dazhou (Chinese Research Center for Certified Reference Materials, Beijing 100013): *Chin. J. Environ. Sci.*, **16**(6), 1995, pp. 4—6

Under simulated atmospheric conditions, the photochemical reactions were studied in the four systems of $CH_3Br + H_2O_2 + O_2$, $CH_3Br + O_2$, $CHBr_3 + H_2O_2 + O_2$, and $CHBr_3 + O_2$. Irradiated by UV at 253.7 nm, H_2O_2 in these systems was decomposed to give OH radical which then reacted with CH_3Br and $CHBr_3$. The products of these reactions were determinated with a Fourier Transform Infrared Spectroscopy in a 20 m long path cell. As the products of photochemical reactions, CO, CO_2, CH_2O and H_2O were detected in both systems of $CH_3Br+H_2O_2+O_2$ and CH_3Br+O_2; CO, CO_2 and H_2O were detected in the system of $CHBr_3+H_2O_2+O_2$; and CO and CO_2 wrer detected in the system of $CHBr_3+O_2$. Based on these products, the photochemical reactions which possibly occurred were suggested and reasonable explanations were given.

Key words: photochemical oxidation, OH radical, brominated alkanes.

Biotechnological Removal of Sulfides in the Effluent from Sulfate Reducing Reactors. Zuo Jian'e et al. (Dept. of Environ. Eng., Tsinghua University, Beijing 100084): *Chin. J. Environ. Sci.*, **16**(6), 1995, pp. 7—10

Studies have been carried out on the possiblity of converting sulfides directly by colourless sulfur bacteria into elemental sulfur in the treatment of effluent from sulfate reducing reactors. The treatment was conducted in an upflow biofilm reactor packed with Rasschig rings at an ambient temperature (18—22°C). The results show that sulfides were removed at a rate of over 90% and almost all of sulfides removed were coverted into elemental sulfur while organics being removed at a rate of about 10% only, when the treatment was conducted with a sulfide volumetric loading of 12 kg $H_2S/(m^3 \cdot d)$, a hydraulic retention time of 22 minutes and a dissolved oxygen (DO) concentration of 5.0—5.5 mg/L and at a pH value of 7—8. The results also show that the DO concentration required in the biofilm reactor and the increase in pH value were linearly correlated to the sulfide loading in the influent and to the amount of sulfides removed, respectively.

Key words: aerobic microbial desulfurizing process, upflow aerobic biofilm reactor, colourless sulfur bacteria, elemental sulfur.

Alleviating Effect of Silicon on Aluminum Toxicity to Wheat Growth in Acid Soil. Huang Qiaoyun et al. (Dept. of Soil Science, Huazhong Agricultural University, Wuhan 430070): *Chin. J. Environ. Sci.*, **16**(6), 1995, pp. 11—13

Pot culture experiments were carried out to study the effect of silicon application in acidic soil on the