水中六六六与五氯苯酚的光催化氧化 *

李　田　　　仇雁翎

(同济大学环境工程学院，上海　200092)

摘要　以高压汞灯为光源，TiO_2为催化剂，研究了水中低浓度六六六与五氯苯酚的光催化氧化。六六六易被光催化氧化，其4种异构体的半衰期十分接近，均在20 min 左右。pH 中性条件下 γ-六六六的氧化速率较高。六六六光催化氧化存在含氯中间产物，并可逐渐被氧化去除。五氯苯酚光催化氧化速率明显高于光分解。30 min 之内五氯苯酚即可完全脱氯。随反应过程的继续，五氯苯酚被氧化成简单的小分子直至完全矿化。该法在饮用水深度处理中有良好的应用前景。

关键词　光催化氧化，六六六，五氯苯酚。

近10年来国内外对多种类型有机物的光催化氧化进行了研究[1]。而六六六(BHC)的光催化氧化未见报道。六六六的4种异构体均为可疑致癌物，属美国环保局确定的129种优先考虑污染物。五氯苯酚(PCP)广泛用作杀菌剂和木材防腐剂，是致突变物。世界卫生组织建议饮用水中五氯苯酚的含量不超过10 μg/L。Massimo B. 等曾研究过 PCP 的光催化降解[2]。国内对之尚缺乏研究。

1　试验装置及方法

1.1　试验装置

试验在容积2 L 的圆柱状间歇反应器中进行。反应器中央是石英玻璃冷却套管，套管中插有作为光源的 GGZ125 直管型高压汞灯。调节流过套管夹层的冷却水的流量，可使反应过程中溶液温度保持在25±1℃之间。用电磁搅拌器使催化剂均匀悬浮。通过反应器上的旋塞取样分析。

1.2　试剂

BHC 4种异构体均为分析纯，由成都第二化学试剂厂生产。PCP 是青浦新产品研究所出品的化学纯试剂。催化剂为 E. Merck 公司生产的分析纯 TiO_2，经测定其晶型为锐钛型。

1.3　分析方法

BHC 经石油醚萃取后，用北京分析仪器厂生产的 SP2308 气相色谱仪，^{63}Ni 电子捕获检测器测定。色谱柱为5％OV-17＋Chromosorb WAW 60—80目。PCP 用751G 分光光度计，在220 nm 处测定消光值定量。Cl^- 用 Dionin 2020 i 离子色谱仪，HPIC-AS4A 分离柱测定。

1.4　试验操作

以去离子蒸馏水配成反应液2L，加热到25℃后注入反应器。加入催化剂2 g，并用电磁搅拌器搅拌。高压汞灯预热后插入反应器，定时取样分析。测定 BHC，浊水样先用石油醚萃取，再将分离出的有机相用离心机离心，除去其中水分及 TiO_2。测定 PCP 紫外消光值及 Cl^- 浓度，水样先用离心机澄清，再用0.22 μm 微孔滤膜过滤后供测定。

2　试验结果

2.1　BHC 的处理效果

γ-BHC 的光催化氧化和光分解效果见图1。虽然本试验直接以自来水作冷却剂，没有用滤光液滤除光源发出的紫外光中易引起直接光分解的短波成分，γ-BHC 仍不能被光分解。与之

成为对照，γ-BHC 的光催化氧化却十分迅速，半衰期不到 20 min。进一步的试验表明，BHC 的其它 3 种异构体也都有不能被光分解，但可发生光催化氧化。4 种异构体的光催化氧化在半对数坐标上均呈直线，符合一级反应关系。反应速率常数 K 反映了它们的相对反应速率。在 pH6.2 的条件下，BHC 4 种异构体的光催化氧化效果见表1。由表1可知，BHC 4 种异构体的光催化氧化速率十分接近，其差别与试验误差相当。这说明 BHC 分子空间结构的差异对它们的光催化氧化没有影响。BHC 难为臭氧氧化，不能光分解或生物降解。本研究为去除饮用水中微量 BHC 提供了新的选择。
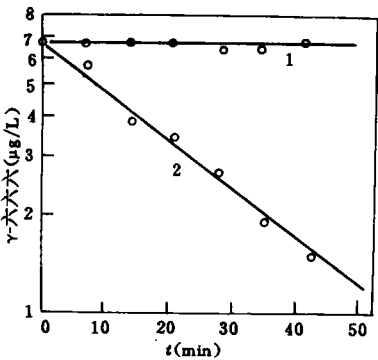

图1　γ-BHC 的光分解与光催化氧化
1. 光分解　　2. 光催化氧化

表1　BHC 4 种异构体光催化氧化速率常数

反应物	α-BHC	β-BHC	γ-BHC	δ-BHC
速率常数(min^{-1})	0.032	0.034	0.035	0.035

　　为确定溶液 pH 对 BHC 光催化氧化的影响，以 γ-BHC 为底物，分别用 H_2SO_4 和 HaOH 调节溶液的 pH 值，测定了不同 pH 条件下 BHC 的去除效果(图2)。图2中 pH 均为反应液的初始 pH 值。反应过程中随着 Cl$^-$ 的生成，溶液的 pH 逐渐下降。试验对反应过程中 pH 的变化未加控制。

　　由图2可见，pH 对 BHC 光催化氧化的影响十分明显。随着 pH 的升高，反应速率迅速提高。而在酸性较强时，光催化反应几乎不能进行。根据以往的研究，pH 对不同类型有机物光催化氧化的影响不同[3, 4]。这说明 pH 影响的程度和趋势不仅与光催化氧化过程的机理有关，也受被氧化物本身性质的影响。在 pH 中性条件下 BHC 的去除效果良好，这对饮用水中微量 BHC 的去除是有利的。
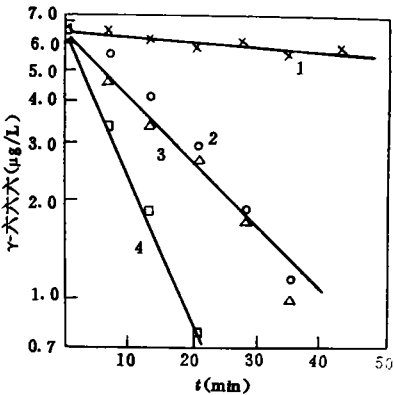

图2　pH 对 γ-BHC 光催化氧化的影响
1. pH3.2　2. pH7.4　3. pH10.6　4. pH12.1

　　BHC 光催化氧化是否存在中间产物及中间产物的毒性，是饮用水深度处理中的一个重要问题。γ-BHC 的溶解度不高，仅 7.9 mg/L，且 BHC 分子中氯占了很大比例，因此直接测定溶液的 TOC 判定 BHC 分子的矿化程度较为困难。本研究在尽可能高的初始浓度下，测定了 γ-BHC 的氧化降解情况，同时使用离子色谱测定反应生成的 Cl$^-$，以确定分子中氯的无机化程度及是否有含氯中间产物生成。试验结果见图3。试验表明，在接近饱和溶解度的条件下，γ-BHC 的氧化降解规律没有明显变化，与 μg/L 时相近。即在其溶解度范围内，γ-BHC 的光催化氧化半衰期与起始浓度无关。由图3可见，BHC 分子的破坏和分子中氯的无机化并非同步发生。这说明有新的氯化有机物生成。新生成的氯化有机物也可被光催化氧化。氯的完全无机化(>95%)可经较长时间的反应达到。一般认为，同类氯化有机物的毒性是随分子中氯含量的减少而下降的。比较图3中氯离子的实测值和理论生成值可知。在 BHC 分子被破坏的同时，分子中大部分氯已成为 Cl$^-$ 被释放。这意味着即使生成了新的氯化有机物，其毒性很可能是小于 BHC 的。
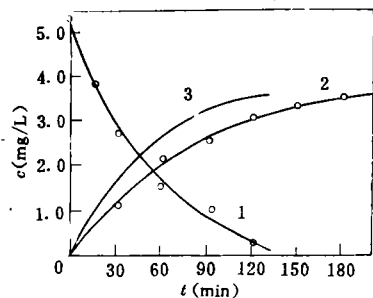
图3 BHC 的光催化氧化与脱氯
1. BHC 2. Cl⁻实测值 3. Cl⁻理论生成量

2.2 PCP 的光催化氧化

在初始 pH5.6 条件下，PCP 的光催化氧化和光分解情况见图4。图4表明，PCP 有明显的光分解，不过其反应速率大大低于光催化氧化。本研究以高压汞灯为光源（E_{max} 365 nm），直接用自来水冷却，所以有波长＜300 nm 的短波紫外光进入反应液，引起 PCP 的光分解。可以认为，PCP 光催化氧化的实测结果基本上不受光分解的干扰。理由是在催化剂用量1 g/L 时，浊液中紫外光的透射深度极小，只有3—4 mm，光分解难以发挥作用，而且光分解过程的反应速率本身又小于光催化氧化。
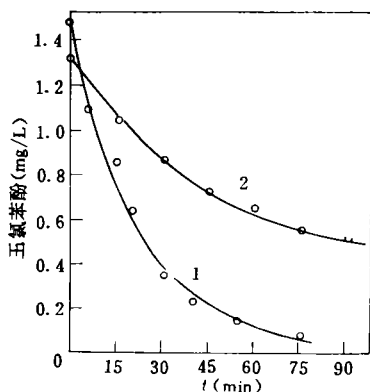

图4 PCP 的光催化氧化与光分解
1. TiO₂（1 g/L） 2. 无催化剂

在较高的初始浓度下，测定了 PCP 的氧化与脱氯，试验结果见图5。由图5可见，PCP 的脱氯在30 min 之内就达到了100％。这说明图4中根据紫外吸光值推算出的某一时刻下 PCP 的剩余浓度值偏高。PCP 完全脱氯后，还有不含氯

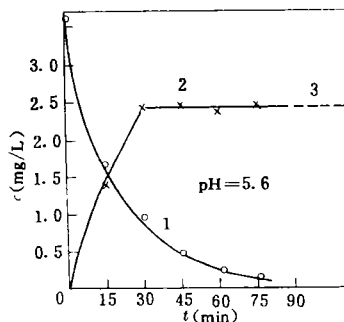的中间产物存在。图5中反应物的消失，实际上是连同吸收紫外的中间产物（如不饱和羧酸）也都被氧化去除。根据笔者对苯酚及氯苯光催化氧化的研究[5]，随着反应的继续，开环后的 PCP 同其它芳香化合物一样，将逐渐被完全氧化为无机物。

图5 PCP 的脱氯
1. PCP 2. Cl⁻ 3. 理论生成量

3 结论

（1）BHC 的4种异构体均不能被光分解，而易为光催化氧化。4种异构体的氧化速率基本相同。γ-BHC 的光催化氧化存在含氯中间产物。随反应过程的继续，生成的氯化中间产物也被完全去除。

（2）pH 值对 BHC 光催化氧化有明显影响。酸性条件下，γ-BHC 难以氧化。随 pH 的升高，反应速率迅速上升。在中性范围内，BHC 的光催化氧化情况良好。

（3）PCP 易被光催化氧化，其反应速率远高于直接光分解。氯离子的生成量很快达到理论极限值。因此确定 PCP 的光催化氧化过程中无有害的氯化有机物生成。

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that PCP removal by granular sludge in UAD reactors was due to biodegradation rather than adsorption and volatilizaiton.

Key words: pentachloropenol, biosorption, de-sorption, biodegradation, anaerobic.

Photocatalytic Oxidation of Benzene Hexachloride and Pentachlorophenol in Aqueous Solution.

Li Tian and Qiu Yanling (School of Environ. Eng., Tongji Univ., Shanghai 200092); *Chin. J. Environ. Sci.*, **17**(1), 1996, pp. 24—26

Photocatalytic oxidation of low concentration of benzene hexachloride (BHC) and pentachlorophenol (PCP) in aqueous solution is studied with a high pressure mercury lamp as radiation resource and TiO_2 as a catalyst. BHC can be oxidized easily, half life periods of the 4 isomers of BHC are all around 20 minutes. Oxidation rate of γ-BHC is higher under neutral condition. Chlorinated medium products formed in the photocatalytic oxidation of BHC can be gradually removed by further reaction. For PCP reaction rate of photocatalytic oxidation is much higher than that of photolysis. Dechlorination of PCP can be completed within 30 minutes. As the reaction process continues, PCP will be oxidized into simple small molecules and finally mineralized completely. It is predicable that photocatalytic oxidation has bright prospect in advanced treatment of drinking water.

Key words: photocatalytic oxidation, benzene hexachloride, pentachlorophenol, aqueous solution.

The Dissipation and Residue of Quinclorac in Rice Field Water, Soil and Rice Plant.

Wang Yiru et al. (Institute of Agro-environmental Protection, Tianjin 300191); *Chin. J. Environ. Sci.*, **17**(1), 1996, pp. 27—30

Quinclorac is a new herbicide with high efficiency and low toxicity. The field experiments were carried out both in Tianjin and Jilin Province in 1993 and 1994, respectively. It has been found that the herbicide dissipated rapidly from water and leaves. Its half life values in the water was 0.8 days in Tianjin and 2 days in Jilin, and the half life in rice leaves was less than 1 day. The residure in sediment remained quite low during 6 days of half life. No metabolite was detected in soil. Applied to rice field as a 50% WP formulation at the recommended rates of 412.5 g—525 g/hm², one application, preharvest interval 96—105 days, the residue remaining in unpolished rice was less than 0.005 mg/kg, far below MRL, and was safe to humanbeing.

Key words: Quinclorac, metabolite, dissipation, final residue, water, rice, soil.

Wet Air Oxidation Treatment of H-acid Production Waste Liquor.

Wang Yongyi et al. (Dept. of Environ. Eng., Tsinghua Univ., Beijing 100084); *Chin. J. Environ. Sci.*, **17**(1), 1996, pp. 31—33

Under the condition of reaction temperatures of 200—250℃, initial oxygen partial pressures of 1—3 MPa, the wet air oxidation (WAO) of H-acid has 2-step process, including rapid reaction step, in which during the first 10 minutes after the beginning of the reaction COD is decreased rapidly, and UV/Vis. absorbance is increased drastically at first and then reduced rapidly, and slow reaction step, in which, both COD and UV/Vis. absorbance are decreased slowly during about 20 minutes.

WAO treatment can improve biodegradability of H-acid significantly. After 1 hour reaction carried out at 160 C and 3 MPa initial oxygen pressure, COD was decreased by 50%, and the BOD_5/COD ratio of 10 g/L H-acid solution was increased from 3.4% to 33.3%. The offgas from the WAO treatment of H-acid contains undetectable amount of SO_2 and nitrogen oxides.

Key words: wet air oxidation, H-acid, biodegradability.

Emission Factors of Trace OCS from Crop Residues Burning and Estimation Its Amount in China.

Cao Meiqiu and Zhuang Yahui (Research Center for Eco-Environmental Sciences, CAS, Beijing 100085); *Chin. J. Environ. Sci.*, **17**(1), 1996, pp. 34—36

A method of sampling and analysis for trace carbonyl sulfide has been described. The sample is trapped and concentrated at temperature of liquid N_2 and liberated directly into a gas chromatographic column. The concentration of OCS in compressed air as determined as 2.94×10^{-3} μg/L. The method accuracy expressed in term of standard deviation coefficient is $\pm 0.72\%$. The emission factors of carbonyl sulfide, which were measured during the combustion of rice straws, maize stalks and wheat stalks in an enclosed combustion system, are 1.80, 2.75 and 2.05 g/t for rice straws, maize stalks, and wheat stalks, individual. Standard deviation coefficient are $\pm 6.67\%$, $\pm 8.36\%$, and 9.27% for rice straws, maize stalks, and wheat stalks, respectively. Distribution of the amount of crop residues burned in China is presented with a resolution 1° latitude × 1° longitude. The amount of trace OCS could be calculated with their emission factors.

Key words: carbonyl sulfide, biomass buring, emission factor.

The Study of Trace Elements in Human Hair from the Area of Endemic Arsenism.

Jiang Ling et al. (Institute of Environ. Medicine, Tongji Medical Univ., Wuhan 430030); *Chin. J. Environ. Sci.*, **17**(1), 1996, pp. 37—39

217 hair samples and environmental samples from endemic arsenism in Linhe, Inner Mongolia were analyzed. The results showed that the levels of As, Cu and K in hair in studied area were higher than that in control area, but Zn and Se was opposite. The relationship between the typical symptoms of arsenism and the levels of As, Cu, K and Se in hair were found. There were rank correlations between the concentration of Se, Zn, Cu in hair and As in hair (the coefficient = −0.988, −0.794, 0.783, respectively).

Key words: endemic arsenism, trace elements, hair.

Research for the Problem about the Environmental Discount Rate.

Wang Yonghang and Fu Guowei (Dept. of Environ. Eng., Tsinghua University, Beijing 100084); *Chin. J. Environ. Sci.*, **17**(1), 1996, pp. 40—43

This paper presents a new formula, which describes the relation between private rate or return and social rate of return. The formula includes two environmental parameters, λ, the fraction of national income spent on environmental investment, and η, the elasticity of environmental improvement with respect to environmental spending. From the formula it can be seen that social rate of return or environmental discount rate should decline systematically over time from the point of view of environmental