水体氯化消毒中对甲基苯胺转化形成三氯硝基甲烷的分子机制

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摘要 饮用水消毒副产物三氯硝基甲烷(TCNM)因在饮用水中被频繁检出且对人体有潜在的毒性效应而成为国内外研究的热点, 但TCNM的形成路径目前尚不十分明确, 苯胺类前驱物转化形成TCNM的潜力和分子机制还未被系统阐明. 基于密度泛函理论计算, 本文研究了水体氯化消毒过程中对甲基苯胺(*p*-toluidine)转化生成TCNM的反应机理及能量关系. 计算表明, 质子化的对甲基苯胺拥有比中性状态更高的反应活性, 其经过 β -羟基化反应形成间二羟基中间体. 该中间体随后脱氢生成双羰基中间体, 进而通过ClO⁻活化开环得到开环中间体, 再经氧化、取代等多步反应得到最终产物TCNM. 该研究从分子水平上揭示了反应过程中分子结构和能量状态的变化特征, 有助于深入研究不同苯胺类前驱物在饮用水消毒过程中形成TCNM的潜力和分子机制.

关键词 三氯硝基甲烷, 氯化消毒, 量子化学计算, 反应机制

为减少饮用水污染, 近年来各国严格限制了三卤甲烷(THMs)、卤乙酸(HAAs)和致诱变化合物(MX)等典型含碳消毒副产物(C-DBPs)在饮用水水质指标中的检出浓度, 并逐渐促进消毒工艺的改进. 现有的消毒方式如氯胺消毒虽然很大程度地降低了THMs、HAAs和MX等C-DBPs的生成^[1], 但也导致出现了毒性更大的含氮消毒副产物(N-DBPs)^[2,3], 如卤代乙腈(HANs)^[4]、亚硝胺(NMs)^[5]、卤代乙酰胺(HAcAms)^[6]和卤代硝基甲烷(HNMs)^[7]等. 这些新兴的N-DBPs是由消毒剂与水体中的溶解性有机质(DOM), 特别是溶解性有机氮(DON)化合物发生反应而形成的, 其中HNMs因对人类健康的潜在高风险性而备受关注^[8~11].

HNMs主要包括一氯硝基甲烷(CNM)、二氯硝基甲烷(DCNM)、三氯硝基甲烷(TCNM)、一溴硝基甲烷(BNM)、二溴硝基甲烷(DBNM)、三溴硝基甲烷

(TBNM)、一溴一氯硝基甲烷(BCNM)、一溴二氯硝基甲烷(BDCNM)和二溴一氯硝基甲烷(DBCNM)等9种化合物(图1). 虽然在饮用水中HNMs含量(一般在ND~10 $\mu\text{g/L}$)比一般受控DBPs, 如THMs(4~164 $\mu\text{g/L}$)和HAAs(5~130 $\mu\text{g/L}$)低^[12,13], 但其毒性却更大. 如TCNM毒性是三氯乙酸的32.6倍, 而TBNM毒性更是达到了三溴乙酸的116倍^[7,14]. 毒理学研究数据显示, HNMs具有很高的细胞毒性、细胞遗传毒性和致突变性^[15], 已被美国国家环境保护局(USEPA)列入了优先控制消毒副产物的最高等级^[16]. 国内外对HNMs的研究起步较晚, 其形成规律和毒理学特征是目前饮用水消毒安全领域的热门研究问题^[9~11].

TCNM是在饮用水中最早被发现的HNMs, 且在一般水体的HNMs生成势中占据主导地位^[17], 因此, 研究人员通常把TCNM作为HNMs的代表性物质进行研究.

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图1 9种HNMs分子结构式

Figure 1 Structure diagram of 9 HNMs

但目前国内外对TCNM的研究主要集中在前驱物识别、形成影响因素和毒理效应等方面,对其在水体中的形成机理尚需进一步深入探索. Luo等人^[13]和Yang等人^[18]研究发现,天然水体中的硝基甲烷、氨基酸、氨基糖、硝基甲烷、硝基酚及藻类等一些含氮物质是形成TCNM的主要前驱物. Bond等人^[19]发现,把氨基酸、氨基糖、甲胺、胞嘧啶和腺嘌呤等一些天然亲水有机物的替代物氯化后能形成较低浓度的TCNM. 而Wang等人^[20]考察了20种常见氨基酸经氯化消毒后形成TCNM的潜力,发现氨基酸侧链的不同对TCNM的形成有很大影响,其中苏氨酸和色氨酸的TCNM形成势最高,甘氨酸也能形成大量HNMs. 这些研究表明TCNM的前驱物种类众多,不同前驱物形成TCNM的潜力也有较大差异,不利于系统揭示水体中TCNM的形成机制.

芳香类有机物是目前水源污染中的主要污染物之一,拥有比天然有机物更大的DBPs形成潜力^[21],而苯胺作为污染源中的代表性芳香类有机物,其经氯化消毒生成DBPs的潜力较高^[21~23]. 前人实验研究表明,硝基苯及一些含氨基的芳香类有机物如胞嘧啶和腺嘌呤等是TCNM的重要前驱物^[19,24,25],且Joo和Mitch^[26]与Yang等人^[27]指出前驱物中的-NH₂基团会被HOCl氧化为-NO₂,有利于TCNM的形成. 此外, Wang等人^[28]发现-NH₂官能团与其他活性官能团形成对位、邻位或间位结构时会增加DBPs的生成活性. 基于以上研究,我们推测苯胺类化合物可能也是TCNM的潜在前驱物,因此选择对甲基苯胺(*p*-toluidine)作为模型化合物探讨其在氯

化消毒过程中形成TCNM的化学机制. 本研究使用密度泛函理论(DFT)计算系统研究了对甲基苯胺在HOCl氧化作用下生成TCNM的分子机制,明确了对甲基苯胺形成TCNM的最优反应路径,构建了完整的化学反应机理和能量关系. 该研究有助于从分子水平上深入理解对甲基苯胺化合物形成TCNM的潜力和分子机制.

1 计算方法与模型

(i) 计算方法. 本研究中的所有DFT计算都采用杂化M062X泛函^[29,30],由Gaussian 09软件包完成^[31]. 构型优化和频率计算都使用6-31G(d,p)基组^[32]. 通过频率计算获得优化构型的吉布斯自由能校正值,并验证优化构型的合理性,其中过渡态鞍点有且只有一个虚频,而反应中间体和产物无虚频. 为了获得更准确的能量数据,在优化构型的基础上使用更高水平的6-311+G(d,p)基组进行单点能计算^[33~35],使用SMD溶剂化模型对水溶剂环境(介电常数 ϵ 为78.4)进行隐性模拟^[36]. 因此,本研究报道的最终能量数据为吉布斯自由能和SMD溶剂化效应校正后的相对单点能.

(ii) 计算模型. 对甲基苯胺分子中氨基上的2个H与苯环不在同一平面上,氨基呈锥形结构. 此外,自然键轨道计算显示,氨基中的N原子不是单一的sp³或sp²杂化,它的杂化状态介于sp²和sp³之间^[37]. 首先研究了中性对甲基苯胺分子与HOCl作用生成TCNM的可能性,计算发现该路径并不能顺利得到目标产物. 因此,我们考虑以质子化的对甲苯胺作为TCNM前驱物. 事实上,HOCl作为一种弱酸,在水环境中可电离出少量H⁺,而对甲基苯胺的氨基是供电子体,可以结合溶液中的游离的H⁺形成-NH₃⁺,该结构比中性氨基具有更高的反应活性.

2 结果与讨论

对甲基苯胺氯化形成TCNM的完整反应路径及相对能量变化如图2所示,其中图2(a)显示了从反应物*p*-toluidine到中间体IM7的反应机制及能量变化. DFT计算表明,模型中的(-NH₃)⁺结构,通过HOCl桥与苯环上的 β -碳位点形成六元环状过渡态反应结构,破坏苯环大 π 键形成 β -羟基化中间体. 溶液中的HOCl分子由于具有弱酸性,会电离出ClO⁻夺取 β -碳位点上的质子形成新的HOCl分子,苯环和氨基结构复原,此时 β -碳位点上仅连一羟基官能团. 重复前述步骤,苯环上的2个 β -碳位点上的氢原子均被置换成羟基基团. 计算表明, β -C₆羟基化

反应的能垒为38.60 kcal/mol, 而 β -羟基化中间体(IM1)的形成会释放26.75 kcal/mol的能量, 有利于随后 C_6 位点上的质子离去。事实上, 优化结果显示 β -羟基碳上的氢原子较之苯环结构完整时与碳原子间键长有所增加, 且不再与苯环结构共平面, 稳定性大幅降低, 因此溶液中游离的 ClO^- 可以轻易夺取该质子, 这是一个本质上无能垒的过程。另一 β -碳(C_2)位点的羟基化过程中过渡态TS2的能垒为42.59 kcal/mol, 形成中间体IM4时放热能量为24.43 kcal/mol(该能量数据相对于IM3给出), 随后 β -羟基 C_2 上的质子也会转移给溶液中游离的 ClO^- 形成新的HOCl分子和相对稳定的双羟基化中间体IM5。

后续反应中, 中间体IM5的 β - C_6 羟基上的氢原子会被HOCl的羟基夺去, 同时HOCl的氯原子加成到苯环的 C_5 原子上, 形成氯取代的 β -碳羰基化中间体IM6。该步反应中, 过渡态TS3的相对能垒为46.48 kcal/mol, 形成IM6放出的能量为35.09 kcal/mol。此外, 上述反应后形成的分子结构显示, 与 C_5 对应的 C_3 位点上会形成新的碳碳双键结构, 该结构不利于重复IM5 $\rightarrow$ IM6的反应步骤得到 C_2 羰基化中间体。因此, β - C_2 羰基化反应只能借助 NH_2 来完成, 即HOCl中的羟基夺取 C_2 -OH的氢原子, 同时Cl原子夺取 NH_2 上的氢原子, 形成HCl分子和中间体IM7。该过程对应的过渡态为TS4, 活化能垒为28.75 kcal/mol, 释放热量为38.52 kcal/mol。

中间体IM7~IM13的反应机制及能量变化如图2(b)所示。中间体IM7的双羰基结构稳定性较低, 能轻易被水体中游离的 ClO^- 亲核攻击(对应过渡态TS5的能垒为2.90 kcal/mol), 形成负一价中间体IM8, 质子化后形成中间体IM9。该反应能有效弱化六元环稳定性, 进而有利于随后的开环(C_1 ~ C_6 单键裂解)反应。TS6对应开环过渡态, C_1 ~ C_6 单键断裂, 形成开环中间体IM10。该步反应的活化能垒为17.54 kcal/mol, 吸热15.28 kcal/mol。此后, C_6 -OCl基团上的氯原子转移到 C_1 上, 该反应自发进行无能垒, 且放热57.32 kcal/mol。 C_2 位点上可发生与 C_6 位点相似的反应, 即游离的 ClO^- 攻击 C_2 位点形成中间体IM12, 反应能垒为19.55 kcal/mol, 且反应吸热2.42 kcal/mol; 随后 C_1 ~ C_2 单键裂解, 能垒为12.98 kcal/mol, 得到中间体IM13吸热4.91 kcal/mol, 这一过程会发生分子内部的质子转移。需要注意的是, C_2 位点较之 C_6 位点反应的差别在于氯原子的转移过程中, $=NH_2^+$ 上的一个质子会同时转移给 C_6 上的氧负离子形成羟基, 此过程也无能垒, 是一个自发进行的放热反应。

图2(c)显示了从中间体IM13到产物P-TCNM的反

应机制及能量变化。上述反应形成的二氯碳亚胺(IM14)分子结构中, 由于C=N双键具有很强的稳定性而不易被破坏, 为有利于其与HOCl加成反应, 我们考虑使亚氨基质子化从而降低双键稳定性。质子化后的 $Cl_2C=NH_2^+$ 中双键裂解反应的过渡态(TS9)能垒为92.59 kcal/mol, 生成中间体IM15吸热15.40 kcal/mol。该步反应的能垒远高于其他基元反应, 表明C=N双键裂解是整个反应路径的决速步骤。随后, IM15的氨基去质子化形成IM16, 进而与HOCl反应, 生成中间体IM17($Cl_3C-N(OH)_2$)。该过程能垒为25.23 kcal/mol, 放热17.72 kcal/mol。最后, IM17在一分子HOCl协助下脱去HCl和 H_2O , 同时形成目标产物TCNM, 该步骤的活化能垒为48.04 kcal/mol, 且反应放热36.89 kcal/mol。

综上所述, 对甲基苯胺氯化形成TCNM的反应路径非常复杂, 先后经历质子化、羟基化、羰基化、开环等10多个基元反应步骤。其中, 二氯碳亚胺C=N双键裂解的能垒高达92.59 kcal/mol, 远高于其他基元步骤, 表明该反应是整个反应路径中的决速步骤。此外, 虽然C=N双键裂解反应的能垒很高, 但之前的反应步骤基本上都是放热过程, 这在一定程度上有利于C=N双键的裂解。此外, 需要指出, 整个反应过程涉及氨基的多次质子化。该反应能发挥活化氨基氮原子、弱化碳氮间相互作用的重要作用, 可为后续发生在苯环上的一系列反应创造合适的反应前提。因此, 在水体氯消毒的实际过程中, 可考虑适当抑制HOCl的电离, 降低水体中 H^+ 的浓度, 这样可有效降低芳香胺类化合物的氨基的质子化概率, 进而弱化芳香胺转为TCNM的反应活性。

3 结论

基于量子化学计算研究环境污染物的化学转化机制既可以与已有实验结果相互验证和补充, 也能有效预测污染物的环境命运及潜在毒性效应, 进而为污染物的暴露风险评估提供一定的理论基础。此外, 虽然前人研究已经指出在水体氯化/氯胺化消毒过程中一些稳定的芳香类化合物如硝基酚、苯胺、胞嘧啶和腺嘌呤等是TCNM的潜在前驱物。但截至目前, 不同芳香类化合物转化形成TCNM的潜力和具体反应路径并没有被明确揭示, 这在一定程度上不利于准确识别TCNM前驱物, 也不利于合理评估水体中不同HNMs的生成势。

本研究以天然水体中经常检出的对甲苯胺为前驱物, 首次基于DFT计算模拟了氯化消毒过程中对甲苯

图2 (网络版彩色)对甲苯胺氯化形成三氯硝基甲烷的自由能剖面图及分子机制(能量单位为kcal/mol). (a) 反应物 p -toluidine → 中间体IM7; (b) 中间体IM7 → 中间体IM13; (c) 中间体IM13 → 产物P-TCNM

Figure 2 (Color online) Free energy profile (kcal/mol) and molecular mechanism for TCNM formation from *p*-toluidine. (a) Reactant *p*-toluidine → intermediate IM7; (b) intermediate IM7 → intermediate IM13; (c) intermediate IM13 → product P-TCNM

胺转化形成TCNM的分子机制, 揭示了该反应的详细路径及能量信息. 计算表明, 氨基质子化的对甲苯胺比中性状态具有更高的反应活性. 质子化的对甲苯胺首先发生 β -碳位点的羟基化反应, 形成双羟基化的对甲苯胺中间体, 然后HOCl继续氧化 β -C的羟基位点, 形成氯取代的 β -羰基中间体. 随后, ClO^- 亲核攻击 β -碳位点从而提高 β -碳原子的反应活性, 使得六元环上的碳碳

单键更容易断裂生成二氯碳亚胺中间体, 而后经历 $\text{C}=\text{N}$ 双键断键氧化、氢原子取代、羟基氧化等连续反应生成目标产物TCNM. 整体来看, TCNM形成是一个持续大量放热的反应过程. 综上所述, 本研究从分子水平上详细揭示了对甲苯胺氯化形成TCNM的反应机理及相关能量信息, 可为深入研究其他芳香胺类前驱物形成HNMs的潜力和化学机理提供理论指导.

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Summary for “水体氯化消毒中对甲基苯胺转化形成三氯硝基甲烷的分子机制”

Molecular mechanism of trichloronitromethane formation from *p*-toluidine during chlorine disinfection of water

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In recent years, the nitrogenous disinfection by-products (N-DPBs), such as halonitromethanes (HNMs), haloacetonitriles (HANs) and haloacetamides (HAcAms), have attracted strong interest due to their frequent detection in drinking water and potential toxicological effects on humans. The N-DPBs are generally formed from the reactions of disinfectants with the dissolved organic matter (DOM), especially the dissolved organic nitrogen (DON) compounds in water. Among the unregulated N-DPBs, halonitromethanes (HNMs) have raised great concern because of the potential higher cytotoxicity, genotoxicity, and mutagenicity than the regulated carbonaceous disinfection by-products (C-DBPs). As the earliest and most frequently detected HNM species in drinking water, trichloronitromethane (TCNM) dominates the formation potential of HNMs, and thus it is generally used as a representative species to investigate the HNM formation and toxicological effects. At present, although some TCNM precursors have been specifically identified, the relevant reaction mechanisms are not very clear. Moreover, the formation potential and mechanism of TCNM from aniline precursors have not been definitely elucidated yet. In this work, the density functional theory (DFT) calculations were performed to unravel the mechanistic details of TCNM formation from *p*-toluidine during the water disinfection with chlorine. All DFT calculations were carried out using the hybrid M062X functional implemented in Gaussian 09 program. The 6-31G(d,p) basis set was used for geometry optimizations and frequency calculations, while the larger 6-311+G(d,p) basis set was employed to obtain more accurate single-point energies for all the optimized geometries. The SMD solvation model was further used to implicitly simulate the aqueous environment (dielectric constant $\epsilon = 78.4$). The final energetic data reported in this work are relative free energies estimated by combining single-point energies with SMD solvation effects and Gibbs free energy corrections. We first investigated the possibility of TCNM generation from neutral *p*-toluidine during chlorine disinfection of water, but the results suggested that this pathway is not accessible to target product. By contrast, the protonated *p*-toluidine has higher reactivity than the neutral form. In fact, HOCl is a weak acid, which can release a small amount of H^+ to protonate the amino group of *p*-toluidine to initiate the reaction in aqueous solution. The calculated results show that the TCNM formation from protonated *p*-toluidine first undergo β -hydroxylation to generate the exothermic dihydroxy intermediate, followed by the dehydrogenation to form β -carbonyl intermediate. The subsequent ClO^- attack on β -carbonyl enhances the reactivity of β -C site and facilitates the cleavage of C–C single bond of six-membered ring to generate a carbonimidic dichloride intermediate. This intermediate then undergoes successive elementary steps comprising of C=N cleavage, H atom substitution, and hydroxyl oxidation to form the target product TCNM. The overall reaction is a strongly exothermic process. Furthermore, the energy barrier of C=N cleavage of protonated carbonimidic dichloride intermediate is calculated to be 92.59 kcal/mol, which is much higher than those of the other elementary steps, suggesting C=N cleavage to be rate-determining step in the whole process. It should also be noted that the reaction process undergoes multiple protonation of the amino group, which plays important roles in activating the amino group and weakening the C–N bond, further facilitating the corresponding reactions on benzene ring. Therefore, the TCNM formation potential from aniline precursors may be reduced through the moderate inhibition of HOCl ionization in aqueous solution. In summary, this study for the first time reveals the complexity of reaction mechanism and the relevant kinetics of TCNM formation from *p*-toluidine at the molecular level, which may provide meaningful guidance for the further studies of formation potential and mechanism of TCNM from other similar aniline precursors during the chlorine disinfection process in drinking water.

trichloronitromethane, chlorination disinfection, quantum chemical calculation, reaction mechanism

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