

大气臭氧损耗中双自由基反应机理的量子化学研究*

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摘要 用量子化学 RHF 理论方法研究了单重态双自由基 NH 、 CH_2 、 CCl_2 与大气臭氧 O_3 的反应机理。在 3-21G 水平上用梯度解析技术优化了上述反应的反应物、中间体和产物构型, 6-31G 或 6-21G 计算能量。得到了各构型的有关结构数据。计算表明: 上述反应分 2 步进行, 双自由基先与 O_3 反应生成稳定的中间体, 然后在光照条件下中间体分解为 HNO 、 H_2CO 和 Cl_2CO 等稳定分子。从动力学看, 2 步反应分别为 $[\pi_{4s} + \pi_{2s}]$ 和 $[\pi_{2s} + \pi_{2s}]$ 反应, 热力学上也是允许的。通过本研究, 试图提供一种不计算反应过渡态, 将热力学分析和 Woodward-Hoffmann 规则相结合研究复杂反应的方法。

关键词 双自由基, 臭氧损耗, 反应机理。

60 年代 Hunt^[1,2], 70 年代 Crutzen, Johnston^[3,4] 和 Stolarski 等^[5,6] 分别研究了自由基 H 、 NO 、 Cl 与 O_3 的反应机理。Molina 等^[7] 提出冷冻剂中的氟氯烃类等气体通过光解可产生 Cl 自由基。之后, 人们又研究了自由基 Br 、 HO 、 NO 、 HOCl 与 O_3 的反应。实验^[8,9] 测量了大量动力学数据, 理论上用量子化学和分子反应动力学方法研究了有关反应^[10-12]。但是氟氯烃类等化合物光解过程中还可能生成 NH 、 CCl_2 、 CF_2 、 CH_2 等双自由基。双自由基与臭氧反应的机理目前尚不清楚。本文用量子化学从头算方法, 研究了单重态双自由基 NH 、 CH_2 、 CCl_2 与臭氧的反应, 优化了反应物、中间体和产物的构型。讨论了双自由基与臭氧的反应机理。

1 计算方法

用限制性 Hartree-Fock 方法(RHF), 在 3-21G 基组下用梯度解析法全优化几何构型。6-31G(或 6-21G)//3-21G 计算能量。几何构型优化收敛限是: 体系中各原子内坐标(键长和键角)上最大力分别小于 $1.2 \times 10^{-2} \text{ eV} \cdot \text{a}_0^{-1}$ 和 $1.2 \times 10^{-2} \text{ eV} \cdot \text{弧度}^{-1}$, 键长和键角分别精确到

10^{-4} nm 和 0.1° , 自洽场收敛限为 10^{-7} , 全部计算用 Gaussian-80 程序完成。

2 计算结果和讨论

2.1 反应物、中间体和产物几何构型

RHF/3-21G 优化反应物、中间体和产物几何构型见图 1。

O_3 分别用基组 3-21G、6-21G、6-31G 进行优化。其中 3-21G 优化结果为 $R_{\text{OO}} = 0.1303 \text{ nm}$, $\angle \text{OOO} = 117.0^\circ$, 与实验值^[13] $R_{\text{OO}} = 0.1272 \text{ nm}$, $\angle \text{OOO} = 116.8^\circ$ 符合较好。

本文只研究单重态双自由基与臭氧的反应, 故反应物 2、3、4 都只给出单重态构型。

5、6、7 这 3 个中间体中, 3 个氧原子与碳原子或 3 个氧原子与氮原子均在同一平面上, 为平面四边形结构, H 或 Cl 原子位于与分子骨架垂直的平面上。与 O_3 相比, 在中间体中键角 $\angle \text{OOO}$ 减小 27° 左右, 键长 R_{OO} 增加 0.02 nm 左右, 几何构型改变不大, 说明形成反应中间体的活化势垒不会太高。

* 国家自然科学基金资助项目

收稿日期: 1995-07-14

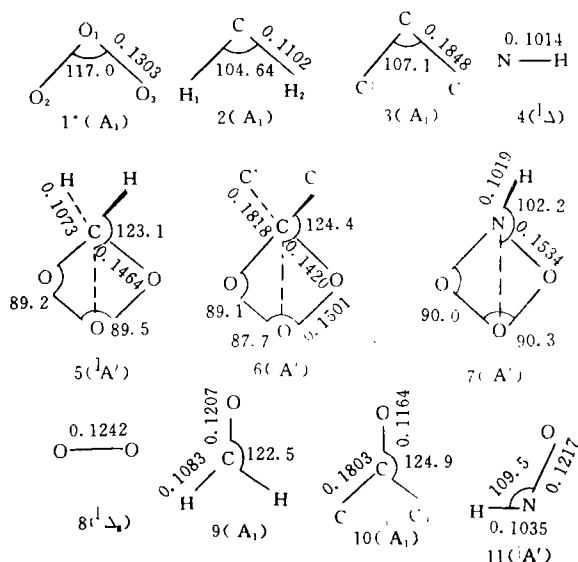


图1 反应物、中间体、产物构型(3-21G)

(键长 nm, 键角°)

*, $O_3(^1A_1)$ 的实验测定数据和其它基组的优化计算

结果: 0.1272 nm, 116.8°(实验); 0.1300 nm,

117.3°(6-21G); 0.1251 nm, 119.6°(6-31G)

表1 O_3 占据轨道和低能虚轨道能级

轨 道	3-21G	6-31G	CCSDT-1-DZP ^[13]
占据轨道			
1a ₁	-20.80589	-20.91803	-20.90473
1b ₂	-20.61343	-20.72940	-20.70969
2a ₁	-20.61300	-20.72923	-20.70963
3a ₁	-1.72351	-1.81491	-1.73644
2b ₂	-1.40981	-1.47750	-1.42448
4a ₁	-1.08600	-1.08756	-1.10125
5a ₁	-0.80555	-0.85167	-0.82490
3b ₂	-0.76276	-0.80962	-0.79462
1b ₁	-0.75776	-0.80243	-0.77102
4b ₂	-0.55681	-0.58142	-0.56728
6a ₁	-0.53848	-0.55405	-0.55659
1a ₂	-0.47238	-0.49778	-0.48562
空轨道			
2b ₁	-0.05381	-0.05518	-0.05969
7a ₁	0.26781	0.28716	0.26255
5b ₂	0.37547	0.40799	0.34168
8a ₁	1.57368	0.99433	0.69912
6b ₂	1.58128	1.02487	0.74709

产物 8、9、10、11: O_2 为单线态, H_2CO 、 CCl_2O 、 HNO 均为单重态。

以下将用 Woodward-Hoffmann 规则对产物

电子结构进行分析。

2.2 O_3 的轨道能级

表 1 列出本文计算的臭氧分子轨道能级, 与文献^[13]计算结果相近, 只是较高能级轨道差别较大。

2.3 反应过程的能量变化

表 2 给出了各体系总能量和偶极矩的计算结果, 表 3 给出了各步反应及总反应的能量变化 ΔE , ΔE 定义为 $\Delta E = E(P) - E(R)$, $E(P)$ 和 $E(R)$ 分别表示产物和反应物能量。

由表 3 可知, 生成中间体的反应为强放热反应, 从热力学角度讲, 反应自由能 $\Delta G_0 = \Delta E - T\Delta S$, 尽管反应为减熵过程, 但因 ΔE 负值太大, 故 $\Delta G < 0$, 形成中间体为热力学允许过程, 反应中间体有较高稳定性。中间体分解为弱放热反应, 反应为增熵过程 $\Delta S > 0$, 温度较高时, 反应自由能 $\Delta G < 0$, 也为热力学允许过程。总反应为强放热反应和热力学允许反应。

2.4 电荷分布和前线轨道相互作用

图 2 给出了反应物、中间体和产物的 Mulliken 布居分布。表 4 给出反应物和产物的前线轨道及其能级。

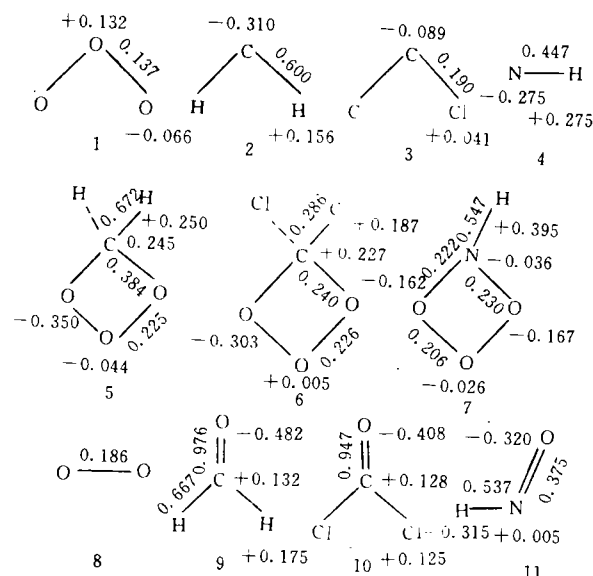


图2 反应物、中间体和产物的 Mulliken 布居分析(3-21G)

表 2 反应物、中间体、产物总能量(a. u.)和偶极矩(Debye)

体系	总 能 量		偶 极 矩	
	3-21G	6-31G(6-21G)	3-21G	6-31G(6-21G)
1	-222.989216	-224.011543 (-223.786044)	0.504	0.057 (0.142)
2	-38.651845	-38.853359	2.196	2.239
3	-952.103805	(-956.591725)	0.124	0.037
4	-54.548659	-54.835558	1.816	1.974
5	-261.923498	-263.230514	3.385	3.654
6	-1175.325525	(-1180.718370)	0.873	0.782
7	-277.721148	-279.089176	2.483	2.645
8	-148.687199	-149.458198 (-149.298604)	0.0	0.0 (0.0)
9	-113.211820	-113.808272	2.659	3.032
10	-1026.648014	(-1031.435368)	0.615	0.660
11	-129.108290	129.712884	2.242	

表 3 各反应的能量变化(kJ/mol)¹⁾

化 学 反 应	$\Delta E(3-21G)$	$\Delta E(6-31G$ 或 6-21G)
$O_3 + CH_2 \longrightarrow O_3CH_2$	-741.43	-959.80
$O_3 + CCl_2 \longrightarrow O_3CCl_2$	-610.37	(-894.15)
$O_3 + NH \longrightarrow O_3NH$	-481.13	-635.50
$O_3CH_2 \longrightarrow O_2 + CH_2O$	64.26	-94.39
$O_3CCl_2 \longrightarrow O_2 + CCl_2O$	25.43	(-40.96)
$O_3NH \longrightarrow O_2 + HNO$	-195.16	-215.02
$O_3 + CH_2 \longrightarrow O_2 + CH_2O$	-677.17	-1054.20
$O_3 + CCl_2 \longrightarrow O_2 + CCl_2O$	-635.8	(-935.10)
$O_3 + NH \longrightarrow O_2 + HNO$	-676.29	-850.51

1) 括号内值为 6-21G 计算结果

表 4 反应物、产物前线轨道及能量(3-21G)

体系	轨道类型	轨道能级	FMO(仅列出主要项) ¹⁾
O_3 (1A_1)	NHOMO(a_1)	-0.538	$-0.556O_1(2P_x) + 0.741O_2(2P_z) - 0.741O_3(2P_z)$
	HOMO(a_2)	-0.472	$-0.822O_2(2P_x) + 0.822O_3(2P_x)$
	LUMO(b_1)	-0.054	$0.853O_1(2P_y) + 0.717O_2(2P_y) - 0.717O_3(2P_y)$
CH_2 (1A_1)	HOMO(a_1)	-0.376	$-0.637C(2s) + 0.885C(2P_z)$
	LUMO(b_1)	0.076	$1.026C(2P_x)$
CCl_2 (1A_1)	HOMO(a_1)	-0.433	$-0.504C(2s) - 0.645C(2P_z) + 0.778Cl_1(3P_z) + 0.778Cl_2(3P_z)$
	LUMO(b_1)	-0.005	$1.152C(2P_x) - 4.404Cl_1(3P_x) - 0.404Cl_2(3P_x)$
NH ($^1\Delta$)	NHOMO	-0.530	$0.665N(2s) - 0.791N(2P_z) - 0.493H(1s)$
	HOMO	-0.420	$1.039N(2P_x) + 0.486N(2P_z)$
	LUMO	0.080	$-0.483N(2P_x) + 1.029N(2P_z)$
O_2	HOMO	-0.477	$-0.764O_1(2P_x) - 0.495O_1(2P_z) + 0.764O_2(2P_x) + 0.495O_2(2P_z)$
	LUMO	0.027	$-0.500O_1(2P_x) + 0.873O_1(2P_z) + 0.500O_2(2P_x) - 0.873O_2(2P_z)$
H_2CO	HOMO(b_2)	-0.473	$0.211C(2P_x) - 0.983O(2P_x) - 0.364H_1(1s) - 0.364H_2(1s)$
	LUMO(b_1)	0.147	$1.052C(2P_x) - 0.983O(2P_x)$
Cl_2CO (1A_1)	HOMO(b_2)	-0.476	$0.255C(2P_z) - 0.627O(2P_z) - 0.706Cl_1(3P_z) - 0.706Cl_2(3P_z)$
	LUMO(a_1)	0.064	$-0.703C(2P_z) - 0.380C(2s) + 0.235O(2P_z) - 0.673Cl_1(3P_z) - 0.673Cl_2(3P_z)$
HNO	NHOMO(a'')	-0.580	$0.667N(2P_y) - 0.787O(2P_y)$
	HOMO(a')	-0.420	$0.404N(2s) - 0.512N(2P_z) - 0.492N(2P_x) - 0.394O(2P_x) + 0.807O(2P_z)$
	LUMO(a'')	0.100	$-0.992N(2P_y) + 0.921O(2P_y)$

1) 价原子轨道系数为内外层之和

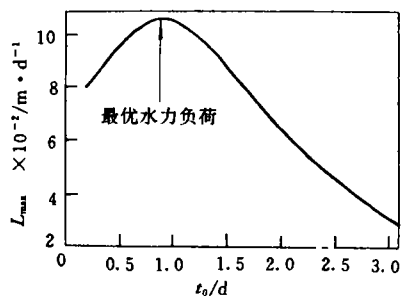
从表 4 可以看出,在形成中间体的过程中, O_3 的最高和次高占据轨道(HOMO, NHOMO)均为价轨道,参与了反应过程中旧键的断裂和新键的生成。这 2 个轨道均为 π 型轨道,可以看成是一个 π_3^4 键。双自由基最高占据轨道上有一孤电子对,因此形成中间体的反应为 $[\pi_{4s} + W_{2s}]$ 型反应,符合 Woodward-Hoffmann 规则,为动力学允许的反应过程,这类反应可以看成是推广的 Diels-Alder 反应。

由图 2 可以看出,形成中间体的过程中,电子从双自由基流向 O_3 ,使得中间体中 O_3 部分负电荷增大,正电荷减小,双自由基部分负电荷减小,正电荷增大,并且发生了较大电荷流动。

说明形成中间体时,双自由基最高占据轨道(HOMO)与 O_3 的最低空轨道(LUMO)有较强的相互作用。

尽管中间体有较高的稳定性,但在光照条件下可以发生裂解。有 2 种裂解方式,1 种是还原为反应物,另 1 种是生成 O_2 、甲醛或二氯甲醛,如表 3 第 2 组反应所示。这些产物都是已知的稳定分子。前面已经说明,从热力学上看,这些反应是能够发生的。另一方面,这些反应可以看成是 $[\pi_{2s} + \pi_{2s}]$ 型加成反应的逆反应。在光照条件下,中间体变成激发态,然后按 $[\pi_{2s} + \pi_{2s}]$ 方式分解为产物。符合 Woodward-Hoff-

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图3 $t_0-L_{\max}$ 曲线

结果表明,当 $t_0=0.8$ d, 淹水期 1.78 d, 落干期 2.77 d 时, 水力负荷最高, 为 0.1046 m/d, 最优水力负荷周期为 1.78 d 淹水, 2.77 d 落干。

本次试验实际运行时采用 2 d 淹水、5 d 落干的水力负荷周期, 但由于残水(约 20 cm)下渗约需 0.5 天时间, 实际水力负荷周期应为 2.5 d 淹水, 4.5 d 落干。这种运行方式下实际的水力负荷为 0.09 m/d。与计算结果 $t_0=0.5$ d 时, 淹水 2.36 d, 落干 4.55 d, 水力负荷 $L_{\max}=0.0910$ m/d 基本相同, 说明本方法是可行的。根据计算结果, 若试验采用更短的水力负荷周期如 1.78 d 淹水, 2.77 d 落干, 其水力负荷可望有所提高。

4 结论

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mann 规则。为动力学允许过程。

Koopmans 定理指出, 分子轨道能量的负值等于占据该轨道的电子的电离势。因此, 实验上研究双自由基 NH 、 CH_2 、 CCl_2 与 O_3 的反应时, 在光电子能谱上应该能够看到与表 4 轨道能级相应的谱线, 从而证实这些中间体及产物的存在, 并进而证实这些双自由基与 O_3 的反应机制。

3 结论

本文给出一种不计算反应过渡态, 将热力学分析和 Woodward-Hoffman 规则相结合研究复杂反应机理的方法。理论计算表明, 大气中氮氮和氟氯烃等分解生成的双自由基 NH 、

(1) 本文给出了一种以最大水力负荷为目标时水力负荷周期的设计方法。其基本过程是: 当入渗速率递减和恢复曲线已知后, 可使用程序进行计算, 给定不同的 t_0 , 得出相应的 $L_{\max}$ 值, 并据此作 $t_0-L_{\max}$ 曲线, 曲线中的极值点即为最终计算的最大水力负荷, 相应的淹水和落干期就是最优水力负荷周期。

(2) 上述计算的基础是入渗速率递减与恢复曲线, 这些曲线应在实际现场试验中获得。实际结果可能不符合指数或对数曲线而为其它类型的方程, 但其计算方法是类似的。另外, 不同季节时曲线的形状是不同的, 应分别计算。

(3) 迟缓系数 α 的选择具有人为性, 关于迟缓期的确定有待于进一步研究。

(4) 试验结果与计算结果相比表明, 本方法是可行的。

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CH_2 、 CCl_2 等都能与 O_3 发生反应, 从而破坏大气层。有关反应为 2 步反应, 首先臭氧 O_3 与双自由基反应生成较稳定的中间体, 该中间体在光照下分解成产物。

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Province, Danzai Mercury Deposit.

Study on the Catalytically Hydrogenated Conversion of CO₂ Using Ru/Al₂O₃ Catalyst. Zhao Ruilan et al. (Research Center for Eco-Environmental Sciences, Academy of Sciences, Beijing 100085); *Chin. J. Environ. Sci.*, 17(2), 1996, pp. 23–25

In this paper the catalytically hydrogenated conversion of CO₂ was studied using Ru/Al₂O₃ catalyst, the influence of different reaction conditions, such as reaction temperature (260–520 °C, 5000–10000 h⁻¹) and CO₂/H₂ ratio in inlet gas, on CO₂ conversion efficiency and CH₄ formation were reported. At reaction temperature higher than 350 °C the CO₂ conversion efficiency was over 95%, and CH₄ formation rate was about 45%–79%. There was no significant influence on CO₂ conversion efficiency and H₂O formation when the space velocity from 5000 h⁻¹ to 10000 h⁻¹. However, for the CH₄ formation efficiency there was a trough at the space velocity of 7000–9000 h⁻¹. The CO formation changed a little at space velocity of 5000–9000 h⁻¹, but it increased a lot at 10000 h⁻¹. The higher CH₄ formation efficiency was obtained when there existed excess of H₂. The highest CH₄ formation efficiency obtained was 98%.

Key words: carbon dioxide, catalyst, catalytically hydrogenated, methane.

Monitoring on The Concentration of Atmospheric Methane of A Rice Cropping Region in Beijing Area. Cui Ping et al. (Chinese Research Academy of Environmental Sciences, Beijing 100012); *Chin. J. Environ. Sci.*, 17(2), 1996, pp. 26–28

Monitoring on methane concentration in the atmosphere in the rice cropping region was carried out between Oct. 1991 and Nov. 1993. Results indicated that the average concentration of methane of the two testing years in the local region were 1.16 and 1.17 µg/L respectively. The variation of methane concentrations showed a strong seasonal pattern. The concentration and concentration deviation were high in summer and low in winter. During rice vegetation period, the methane concentrations were closely related with the variation of methane emission rates from rice paddies indicating rice paddies is one of the most important methane sources of the region. Running analysis showed that the average increasing rate of atmospheric methane in the region was 0.2%, much lower than some previous reports.

Key words: methane, rice, monitoring, Beijing area.

A simulation Study on the Accumulation of Added Rare Earth Elements in Aquatic Ecosystem. Chen Zhaoxi et al. (Dept. of Chem. Eng., East China Institute of Metallurgy, Maanshan 243002); *Chin. J. Environ. Sci.*, 17(2), 1996, pp. 29–31

The accumulation and distribution coefficients of added rare earth elements (RE) in various parts of simulated aquatic ecosystem were investigated. The results showed that concentrations of added RE in bottom mud and water bodies varied smoothly and in *Lemna minor* and *Cyprinus carpio* varied extremely with the time in the period of experiment. Distribution coefficients of added RE in bottom mud were higher than 96%, in *Lemna minor*, were range of 0.26–1.61%, in water, were range of 0.54%

–0.91%; and in carp were less than 0.035%, but almost on linear increment in the period of experiment. Bio-concentration of added RE in carp was also discussed.

Key words: aquatic ecosystem, accumulation, rare earth elements, bioconcentration.

The Quantum Chemistry Studies of the biradical Mechanism of Destroying Ozone in the Atmosphere. Sun Huabin et al. (Institute of Military Medicine, Jinan Command, Jinan 250014); *Chin. J. Environ. Sci.*, 17(2), 1996, pp. 32–34

The reaction mechanisms of the singlet biradicals NH, CH₂, CCl₂ with ozone in the atmosphere have been studied using RHF method of quantum chemistry. The geometries of the reactants, intermediates and products of the above reactions are optimized with the gradient technique at the 3-21G level, their energies have been calculated at the 6-31G or 6-21G level. The structure data of all species have been obtained. The calculated results show that there are two stages in the above reactions, the reactions of the biradicals with ozone take place first to form the stable intermediates, then the intermediates are decomposed by illuminating to the stable molecules HNO, H₂CO and Cl₂CO etc., respectively. In terms of dynamics two reactions in two stages belong to the types [$\pi_{4s} + W_{2s}$] and [$\pi_{2s} + \pi_{2s}$], respectively, and they are permitted thermodynamically. In this study, a method to investigate complicated reaction based on the combining thermodynamics with Woodward-Hoffmann approach without calculation of transition state was attempted to provide by authors.

Key words: biradical, loss of ozone, reaction mechanism.

The Structure and Toxicity Relationship Study for Nitroaromatics to *Scenedesmus obliquus*. Lu Guanghua et al. (Dept. of Environ. Sci., Northeast Normal Univ., Changchun 130024); *Chin. J. Environ. Sci.*, 17(2), 1996, pp. 35–36

ELUMO, EHOMO, $\Delta(\Delta H_f)$, μ and Q_{NO_2} of 18 nitroaromatic compounds were calculated using the quantum chemical method MNDO. The quantitative structure-activity relationships (QSAR) were developed using the five quantum chemical descriptors for the acute toxicity of nitroaromatics to *Scenedesmus obliquus*. Through step-wise regression analysis, one best equation contained three variables was obtained: $-\log EC_{50} = 2.92 - 0.077\Delta(\Delta H_f) + 0.08\mu + 0.28E_{HOMO}$, $n = 18$, $r = 0.961$, $S = 0.173$. The equation was used to estimate the toxicity of the studied compounds, and the toxic effect was discussed.

Key words: structure, toxicity, nitroaromatics, *Scenedesmus obliquus*.

Effects of Rare-Earth Elements on Growth and Reproduction of *Chlorella pyrenoides*. Hu Qin Hai et al. (Dept. of Environ. Sci., Zhejiang Agricultural University, Hangzhou 310029); *Chin. J. Environ. Sci.*, 17(2), 1996, pp. 37–38

It was studied that effects of rare-earth elements (La, Ce, Pr, Nd and their mixture) on growth and reproduction of *Chlorella pyrenoides*. The results showed that effects of rare-earth elements on growth and reproduction of *Chlorella pyrenoides* were not apparent under lower concentration (2 mg/L), but it was inhibited as the concen-