

Supporting Information

Methane C(sp³)-H Bond Activation by Water Microbubbles

Juan Li^a, Jinheng Xu^b, Qingyuan Song^a, Xinxing Zhang^c,

Yu Xia^{a,b,} and Richard N. Zare^{b,*}*

^a Hubei Key Laboratory of Environmental and Health Effects of Persistent Toxic Substances, School of Environment and Health, Jiangnan University, Wuhan, 430056, P. R. China

^b Department of Chemistry, Stanford University, Stanford, California, 94305, USA

^c College of Chemistry, Key Laboratory of Advanced Energy Materials Chemistry (Ministry of Education), Renewable Energy Conversion and Storage Centre, Tianjin Key Laboratory of Biosensing and Molecular Recognition, Frontiers Science Centre for New Organic Matter, Nankai University, Tianjin, 300071, China

Table of Contents

| | |
|---|----|
| Materials and Methods..... | S2 |
| Table S1. Standard thermodynamic data | S4 |
| Figure S1. Physical picture of microbubble device. | S5 |
| Figure S2. Methane was used as the reaction gas, high-resolution mass spectrometry results of the sample after microbubble treatment (negative ion mode)..... | S6 |
| Reference | S7 |

Materials and Methods

General Details. Chromatography grade deionized water was used for all experiments. Potassium titanium oxalate (PTO), p-carboxyphenylboronic acid, 10-Acetyl-3,7-dihydroxyphenoxazine (ADHP), 5,5-dimethyl-1-pyrroline N-oxide (DMPO) were purchased from Sigma-Aldrich. The purity of all gases used was 99.999%, and they were all purchased from Wuhan Steel Group Gases Co., Ltd (Wuhan, China). The mass spectrometer (Orbitrap Exploris™ 120), the gas chromatograph (TRACE™ 1600), and the ion chromatograph (ICS-6000) were purchased from Thermo Fisher Scientific (Waltham, MA, USA).

Microbubble Generation. The microbubble system consists of a pump, a bubble generator, and an airtight sample bottle. The pump has a flow rate of 40 L/h and the bubble generator was purchased from YLEC consultants (France). Reaction gas is drummed into the sample bottle for 30 min prior to the start of the reaction to displace the original gas in the bottle.

Images of microbubbles were captured by a single-cylinder fluorescence microscope (customized, Guangzhou Mingmei Optoelectronics Technology Co., Ltd., China). Fluorescent images were captured using 570 nm high-luminance green LEDs as the excitation light source, and bright field images were captured using a high-brightness white LED light source. ADHP (10-Acetyl-3,7-dihydroxyphenoxazine) fluorescent probe (10 μM) was pre-spiked in deionized water and green laser excitation was used to obtain the fluorescence images of microbubbles.

Free Radical Analysis. 1 mL of microbubble-treated deionized water was taken at 1 h intervals and mixed with 0.1 M aqueous solution of titanium potassium oxalate in equal volumes, and the absorption spectra of the mixed solutions were detected and compared with their absorbance at 400 nm using a UV-Vis spectrometer. Combined with the standard curve, the concentration of ROS in the system was quantified. Different reaction gases such as air, argon and methane were replaced, DMPO was added to deionized water beforehand, continuous microbubble treatment was performed, and 1

ml of the sample was taken for electron spin resonance spectroscopy (A300-10/12, Bruker, German) to clarify the type of free radicals in the system, and the sample was further examined using high-resolution mass spectrometry to clarify the specific chemical composition.

Quantitative Estimation of Methane Oxidation Products. The volume of the sample bottle is 1 L, deionized water is 300 ml, and the methane (or methane isotope $^{13}\text{CH}_4$) - argon mixture is drummed in until the methane concentration in the sample bottle reaches 1800 ppm. then the microbubbles are started to be drummed in, and at 1h intervals 1 ml of the liquid sample and 2 ml of the gas sample are taken, the liquid sample is detected by the Ion Chromatograph (Negative Ion Mode) and high-resolution mass spectrometry (negative ion mode), and the gas sample is injected directly into the Gas Chromatograph (with flame ionization detector) for component analysis.

Finite Element Simulation. COMSOL 6.1 was used to perform finite element simulations with the multiphase flow portion of the fluid module selected for calculation. The bubble diameter was 100 microns, and the water depth was H (adjustable) and the time for the bubble to rise to the surface was calculated.

This part of the calculation follows Stokes' Law as follows:

$$V_t = \frac{2}{9} \times \frac{r^2 g (\rho_w - \rho_g)}{\mu}$$

where r is the radius of the bubble (100 μm here); g is the acceleration of gravity, taken as 9.81 m/s^2 ; ρ_w is the density of water, taken as 1000 kg/m^3 ; ρ_g is the density of methane, taken as 0.656 kg/m^3 ; and μ is the coefficient of viscosity of water, taken as $0.001 \text{ Pa}\cdot\text{s}$.

Table S1. Standard thermodynamic data[S1-S4]

| Species | ΔH_f (kJ mol ⁻¹) |
|------------------------|--------------------------------------|
| OH ⁻ (aq) | -230 |
| CH ₄ (l) | -74.8 |
| H ⁺ (aq) | 0 |
| H ₂ O (l) | -286 |
| H• (aq) | 201 |
| CH ₃ • (aq) | 138.3 |
| OH ⁻ (g) | 290 |
| CH ₄ (g) | -74.6 |
| H ⁺ (g) | 1150 |
| H ₂ O (g) | -242 |
| H• (g) | 218 |
| CH ₃ • (g) | 146 |

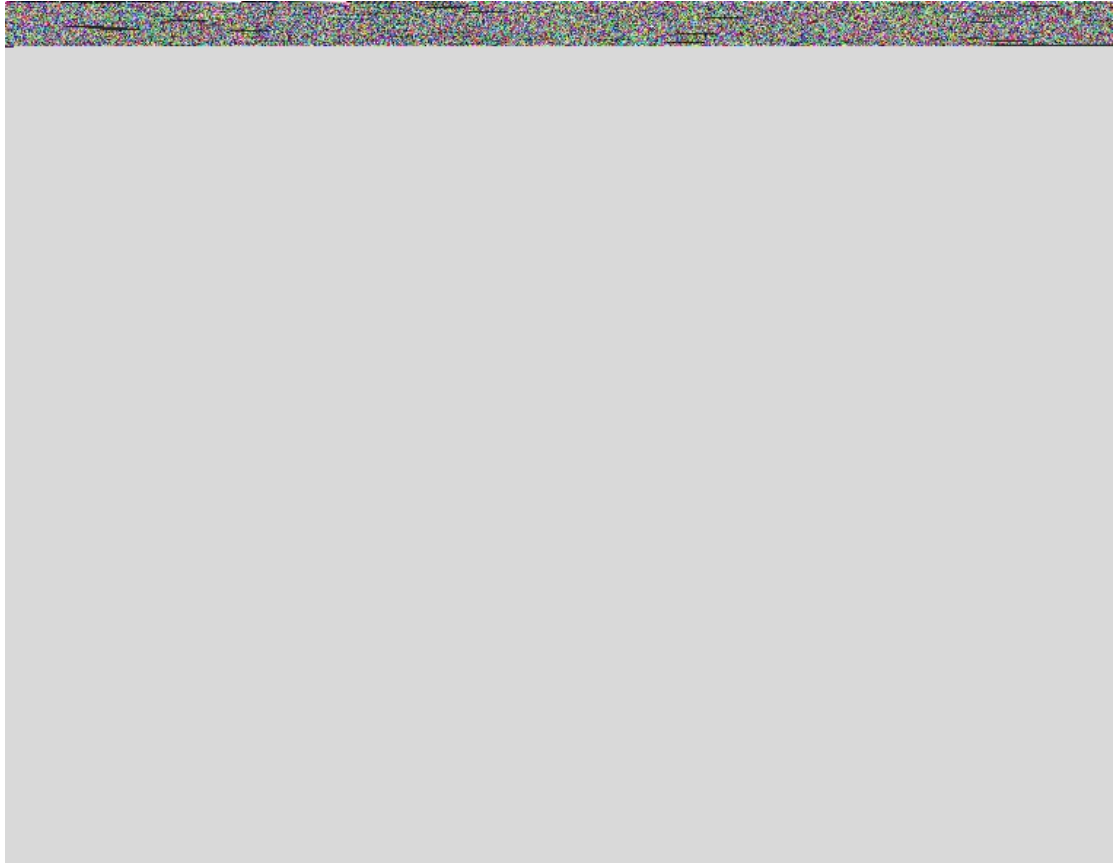


Figure S1. Physical picture of microbubble device.

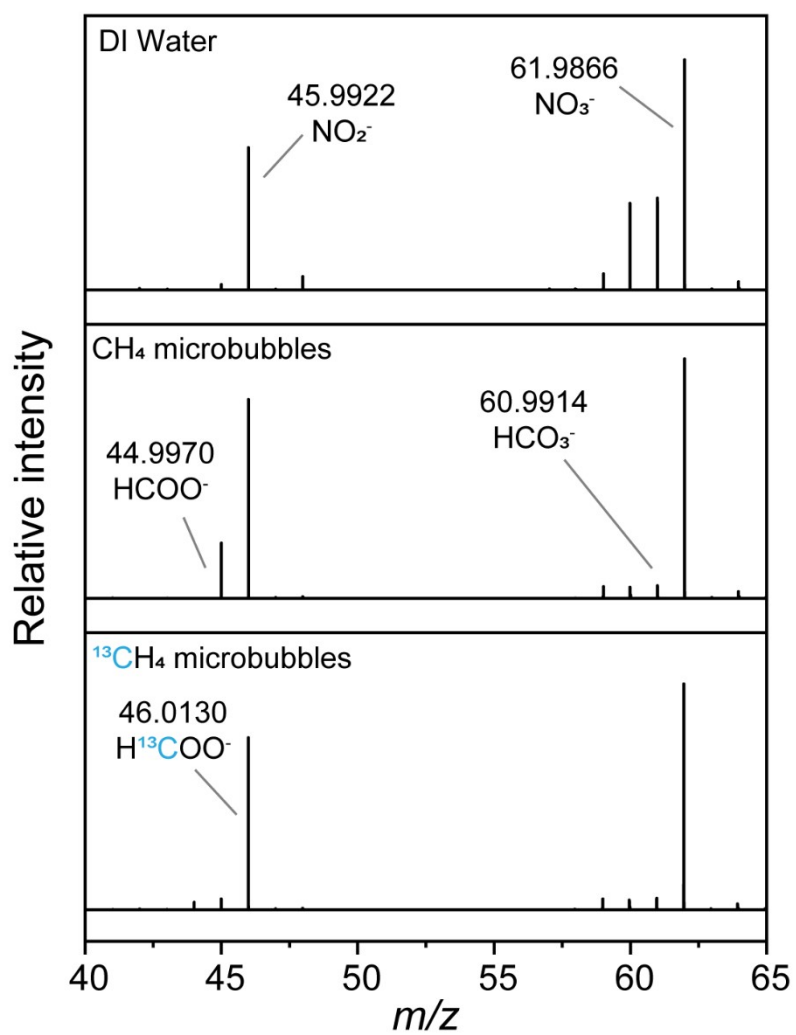


Figure S2. Methane was used as the reaction gas, high-resolution mass spectrometry results of the sample after microbubble treatment (negative ion mode).

Reference

- [S1] https://www.engineeringtoolbox.com/standard-state-enthalpy-formation-definition-value-Gibbs-freeenergy-entropy-molar-heat-capacity-d_1978.html
- [S2] Benson, S. W., Thermochemical Kinetics, 2nd Ed., Wiley, N.Y., 1976, Table A.8.
- [S3] Mejías, J. A., Lago, S., Calculation of the absolute hydration enthalpy and free energy of H⁺ and OH⁻. *The Journal of Chemical Physics* **2000**, *113* (17), 7306-7316.
- [S4] Colussi, A. J., Mechanism of Hydrogen Peroxide Formation on Sprayed Water Microdroplets. *Journal of the American Chemical Society* **2023**, *145* (30), 16315-16317.