

Shinichi Enami

■ **Position /Job Title/Affiliation:** Senior Researcher/
National Institute for Environmental Studies, Japan

■ **E-mail:** enami.shinichi@nies.go.jp

■ **Areas of Expertise:** Atmospheric Chemistry, Physical Chemistry, Interfacial Chemistry



■ Biography (max. 350 words)

2002. 3: Kyoto University, Bachelor of Engineering

2006. 7: Kyoto University, Ph.D (with Prof. Masahiro Kawasaki)

2006. 10 – 2011. 3: California Institute of Technology, Postdoc (with Prof. Michael R. Hoffmann and Dr. A. J. Colussi)

2011. 4 – 2016. 3: Kyoto University, Associate Professor (PI)

2016. 4 – present: National Institute for Environmental Studies, Japan, Senior Researcher (PI)

When I was a student at Kyoto University, I investigated on gas-phase radical-radical reactions using time-resolved cavity ring-down laser spectroscopy. We determined the rate constant for the reaction $\text{IO} + \text{RO}_2$, for example, that play key roles in HOx-cycles in marine boundary layers [1]. Since I joined Caltech as a postdoc, my research topic shifted to interfacial chemistry/physics and aerosol sciences. By using surface-specific online pneumatic ionization mass spectrometry, we have worked on several fascinating topics: ozonolysis mechanism of atmospherically relevant species at the air-water interface [2], lung surface chemistry [3], the acidity/basicity of water interface [4], interfacial Fenton chemistry [5] and so on. I am recently interested in interfacial Criegee intermediate chemistry [6], carbocationic oligomerization at the air-water interface [7], and chemical reactions occurring at microheterogeneous liquid surfaces of internally mixed solvents.

Key References

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Chemical Reactions at Microheterogeneous Aerosol Surfaces

Water is a major component of atmospheric aerosol and living system. However, it is rarely present in pure form but as mixtures with solutes and other solvents. It has been reported that binary mixtures such as water:acetonitrile show abnormal, non-ideal physical properties, that may be related with “microheterogeneity” of internally mixed solutions. Liquid interfaces are where most interesting things happen: some chemical reactions proceed much faster via different mechanisms from bulk media. Especially, the surface microheterogeneity of internally mixed liquid solvents has attracted attentions [1,2]. We address the fact that most liquid interfaces (e.g., the air-aerosol interface) are essentially microheterogeneous. Although this is a general phenomenon of great importance, its effects on chemical reaction mechanisms remain largely unexplored.

Here, we investigate chemical signatures of segregation and differential solvation in fast gas-liquid reactions on aqueous organic mixtures, such as those occurring on tropospheric aerosols and most natural waters. Our probes are very reactive carbonyl oxide diradicals/zwitterions, known as Criegee intermediates (CIs), generated in situ by reacting $O_3(g)$ with a dissolved β -caryophyllene (a C_{15} -diolefin) on mixtures of water (W) with organic solvents (X) of variable composition (X = acetonitrile AN; tetrahydrofuran THF; 1,4-dioxane DIO). Under such conditions, CIs isomerize to functionalized carboxylic acids (FC) or react with interfacial water molecules $(H_2O)_n$ to produce α -hydroxy-hydroperoxides (HH), which we detect by surface-specific online pneumatic ionization mass spectrometry. We found that the dependences of FC and HH formation on molar fraction of bulk water (MF_w) are not smooth but display significant structure, particularly in the case of (water + acetonitrile) mixtures (Fig. 1), which are consistent with the existence of distinct interfacial sub-phases suggested by other techniques. Since CIs are produced from the hydrophobic β -caryophyllene embedded in X-rich X_mW_n clusters, the HH/FC ratio may reflect the composition of clusters (m, n) as a function of MF_w . Our findings show that surface microheterogeneity plays an unanticipated role in atmospherically relevant reactions on the surface of “internally mixed” aqueous/organic aerosol particles.

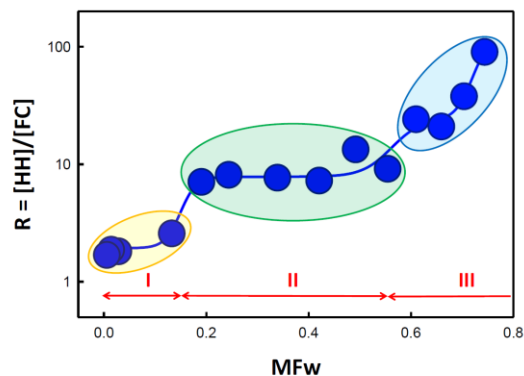


Fig. 1 The ratio R of m/z 305;307 (hydroxy-hydroperoxides, HH) to m/z 251 (functionalized carboxylate, FC) mass spectral signal intensities as a semi-logarithmic function of the molar fraction of bulk water, MF_w , in experiments involving exposing [1 mM β -caryophyllene + 0.2 mM NaCl] in W:AN microjets to $E = 5.3 \times 10^{11} O_3(g)$ molecules $cm^{-3} s^{-1}$. Error bars are within symbols size. Lines are visual guides.

Keywords: aerosol surface, water, microheterogeneity

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