Fundamental Studies of Environmental Chemistry at Air-Water Interfaces

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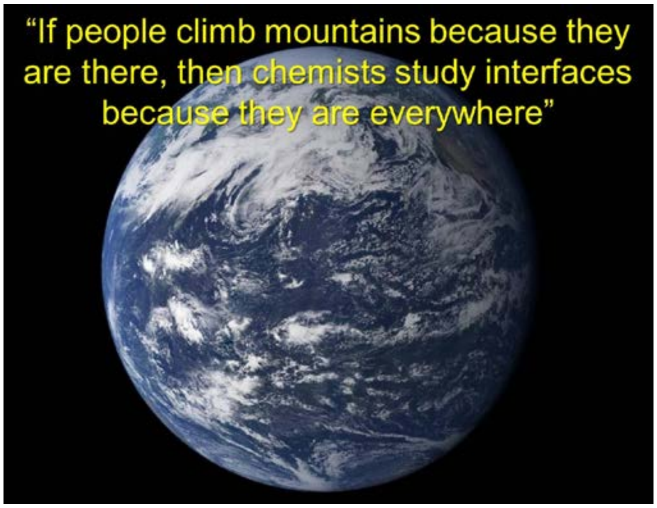

Figure 1. View of Earth from space (credit: NASA). The quote is from Professor Fred Menger, Emory University, Department of Chemistry.

The liquid/vapor interface represents one of the most common chemical environments in nature (Figure 1), present on the surface of oceans and lakes, on atmospheric aerosols, and even in the human respiratory system. Yet in spite of their prevalence, complex reactions occurring at liquid/vapor interfaces remain insufficiently studied and characterized. The technique of field induced droplet ionization or FIDI, developed in our laboratory,[1-3] as a method to examine the composition of interfacial layers, is particularly well suited for fundamental studies of chemical reactions of environmental importance at air-water interfaces. In addition we are employing a novel acoustic droplet ejector[4] to sample interfacial layers from a planar air-water interface. These studies include an examination of highly reactive species such as ozone and OH radicals, key atmospheric reactants such as NO_x and SO_2, and acids (HCl) and bases (NH_3) interacting alone and in combination with organic molecules of environmental interest that have high surface activity. These studies have relevance to problems ranging from environmental chemistry to studies of biological interfaces such as the pulmonary surfactant layer, where we have already made significant progress in understanding the chemical reactions associated with oxidants such as ozone reacting with lipids and proteins in this complex and important interfacial environment.[5-7] Theoretical studies involving state of the art molecular dynamics and quantum chemical calculations play an important role in in these investigations. A key part of the efforts involves development of detailed quantitative models for analyzing the kinetic data obtained in these experiments. This involves full consideration of the uptake of gaseous reactants at the interface and both reaction and diffusion processes at the interface and in the bulk. The discontinuous gas-liquid interface presents an enormous challenge in modeling the chemical reaction dynamics. Importantly, the modeling is constrained by experimental data.

Field Induced Droplet Ionization. Every new method for sampling complex molecules from liquids and solids into the gas phase has fueled the expanding application of mass spectrometry to molecular biology, environmental studies, and other fields of science. Recently developed, field induced droplet ionization (FIDI), combined with mass spectrometric (MS) sampling, holds promise for a broad spectrum of applications.[1-3] FIDI complements techniques such as infrared reflection absorption spectroscopy[8] and sum frequency generation,[9,10] which can also probe interfacial composition and structure, and most importantly allows complex chemical species to be identified and tracked as chemical changes occur at the interface. FIDI-MS involves application of a pulsed high voltage field to a liquid droplet, elongating the droplet to form dual positive and negative ion electrosprays directed opposite to each other. Detailed experiments have completely elucidated the dynamics of this process for both neutral and charged droplets.[2] It is most convenient to form the droplet at the end of a capillary, allow it to become quiescent, and then sample ions from the droplet following a suitable delay to allow for processes of interest to take place involving the droplet, such as the adsorption of molecular species from the atmosphere, or the oxidation of an interfacial layer of oleic acid with ozone (Figure 2).[3] Extensive experiments have shown that when FIDI is carried out just at the threshold for generating the opposing Taylor cones, ions are sampled preferentially from interfacial layers. An example is shown in Figure 3, where a surface active tetraalkylammonium ion is observed to be significantly more abundant than Cs^+, even though the latter is present in 50 fold excess. For comparison, electrospray ionization (ESI) of the same solution exhibits significantly more Cs^+ than is observed with FIDI. The range of interfacial processes that can be studied using the FIDI methodology are shown in Figure 4.

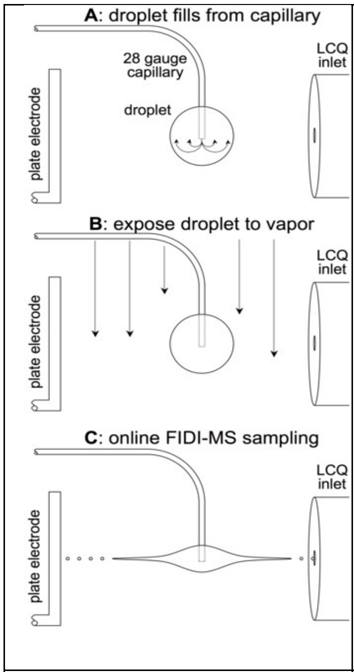

Figure 2. To study interfacial reactions a drop is formed, exposed to reactant vapor, and sampled using FIDI after a suitable period of time.

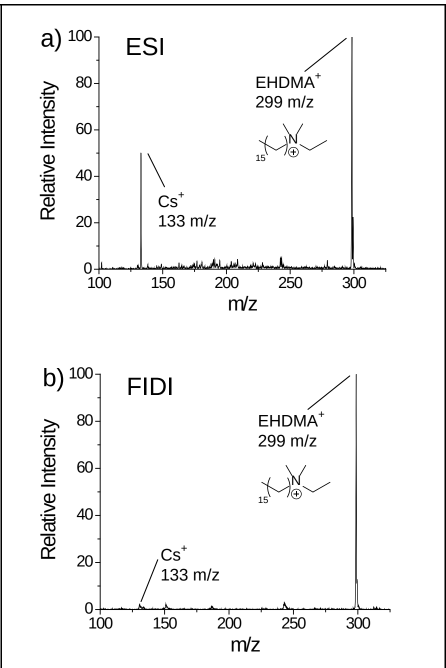

Figure 3. (a) ESI and (b) FIDI mass spectra of 50:1 (29.4μM:0.588 μM) CsI:EHDMA (Ethylhexadecyldimethlammonium) in 1:1 MeOH:H_2O.

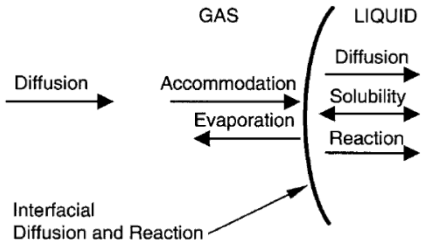

Figure 4. Illustration of interfacial processes that can be studied using FIDI methodology.

Several studies from our laboratory illustrate the ability of FIDI to elucidate complex processes at interfaces, following an initial report of the oxidation of oleic acid by ozone.[3] To illustrate the ability to elucidate details of complex oxidation chemistry, FIDI data for reaction of ozone with the unsaturated lipid POPG in a water/methanol droplet is shown in Figure 5. Reaction intermediates such as hydroxy and alkoxy peroxides are detected, along with a significant yield of the secondary ozonide at m/z 796.[6] This complex chemistry occurs at the surface of the pulmonary surfactant layer in your lung when you breathe ozone.

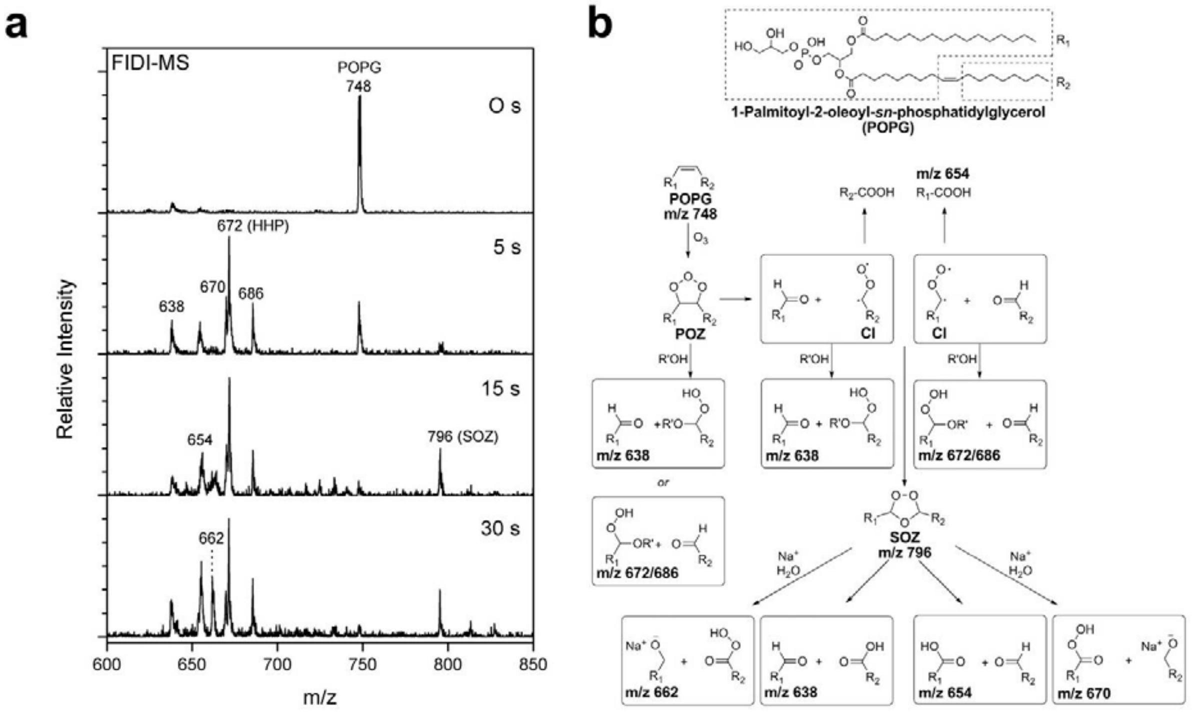

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Figure 5. (a) FIDI data for reaction of ozone (30ppm) with the unsaturated lipid POPG in a water/methanol droplet. (b) Species indicated by their m/z values were all detected in the spectra, including an abundant species at m/z 796, postulated to be the secondary ozonide (SOZ).

Sampling from Planar Liquid Surfaces using Acoustic Droplet Ejection. The FIDI experiments have been expanded to include studies in which surface species are sampled from a planar liquid surface rather than a liquid droplet. We have collaborated with Professor Eun Sok Kim in Electrical Engineering at USC to use his cleverly designed planar focused acoustic wave devices (Figure 6) to eject droplets as small as 0.5 picoliters (Figure 7) from a planar air-water interface.[4] Kim's group has developed a scheme to operate acoustic transducers at higher harmonic frequencies, generating smaller droplets. For focusing acoustic waves, the lens is patterned as Fresnel half-wave bands so that the transmitted acoustic waves arrive at the liquid surface in phase, constructively interfering with each other and intensifying the acoustic pressure, ejecting liquid droplets. These can be directly sampled using our Thermo LTQ mass spectrometer as shown in Figure 8, with excellent signal intensities for individual droplets. We postulate that the focused acoustic pulse leads to shearing of the electrical double layer at the air-water interface, leaving the droplet with a charge and composition representative of the surface active component. We have examined a range of molecular species that have high surface activities, including cationic and anionic surfactants, phospholipids (e.g. Figure 9), and oleic acid. In the case of oleic acid we examined the reaction of ozone at the air water interface with the double bond, obtaining results similar to those obtained with field induced ionization (FIDI). This experimental methodology will make it possible to use a Langmuir trough to vary the lateral surface pressure and examine the effect that this variable has on the surface structure in addition to changes in reactivity due to changes in molecular packing and orientation at the air-water interface.

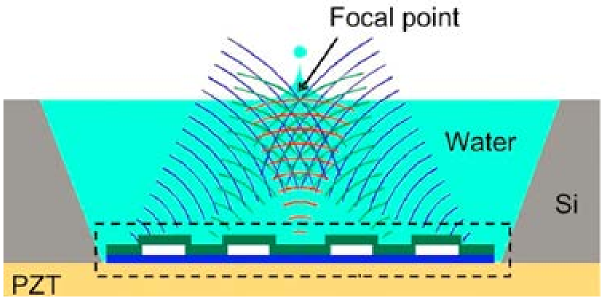

Figure 6. A piezoelectric patterned with a Fresnel lens generates a focused acoustic wave that can eject droplets from an air-water interface at the focal point (Reference 4).

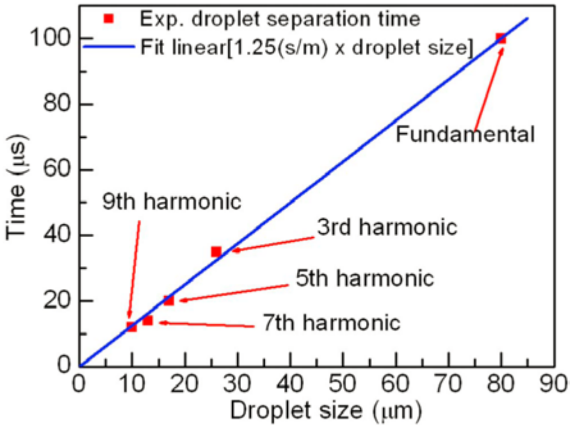

Figure 7. By exciting higher harmonics of the acoustic generator it is possible to sharpen the focal point and reduce the drop size (10 microns corresponds to approximately 0.5 picoliters). (Data from Reference 4).

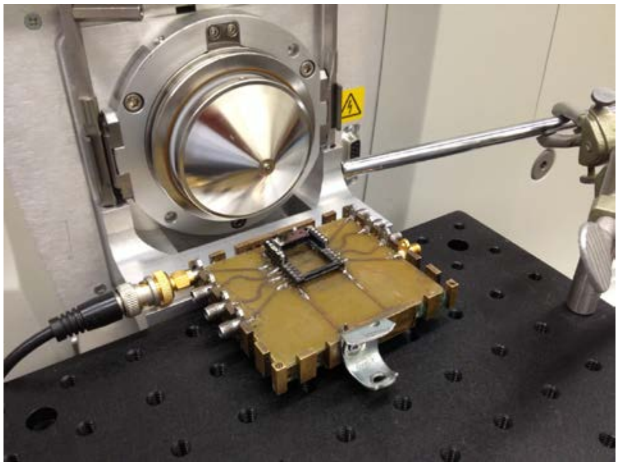

Figure 8. Experimental setup for studying planar liquid surfaces. The acoustic droplet ejector is placed such that the ejected picoliter droplet is directly sampled by the Thermo LTQ mass spectrometer.

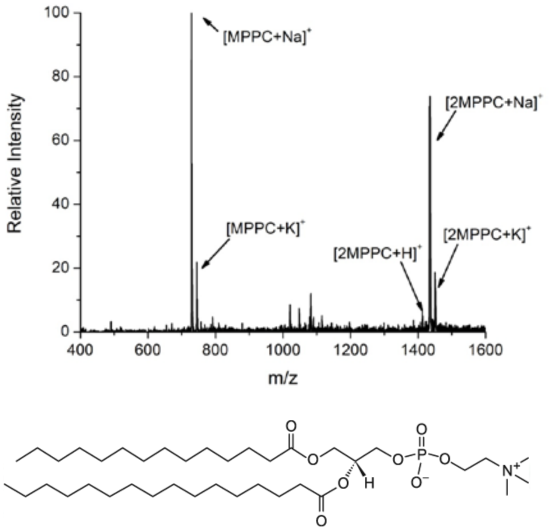

Figure 9. Observed mass spectrum from single droplet acoustically ejected from solution containing the lipid 1-myristoyl-2-palmitoyl-*sn*-glycero-3-phosphocholine (MPPC), 100 μM in 50/50 H_20/MeOH solution.

Also related to these studies, it is known that bursting of bubbles at the ocean's surface not only contributes organic material but leads as well to electrification of the marine atmosphere just above the ocean surface. We have examined the mass spectra of the micron size jet droplets formed by bubble bursting in the presence of ionic surfactants. The spectra observed are very similar to those observed with the acoustic droplet ejector (Byoungsook Goh and Daniel Thomas, unpublished results).

In both the FIDI and acoustic droplet ejector experiments we observe the presence of trace species commonly present in laboratory environments (siloxanes, phthalates used as plasticizers, NO_x, NH_3, etc.). Because of this we have built a completely enclosed system in which the environment around the FIDI droplet or acoustic ejector can be controlled (Figure 10). This will also facilitate the inclusion of environmentally important species such as NO_x and SO_2 as well as acids and bases in the proposed studies. Preliminary studies (Daniel Thomas, unpublished) have been conducted in which exposure of the droplet to acids and bases make it possible to follow the resulting interfacial reaction dynamics over a wide range of time and spatially varying pH at the air-water interface. He recently completed a study of reactions of acid and base-cleavable surfactants with HCl and NH_3, respectively.

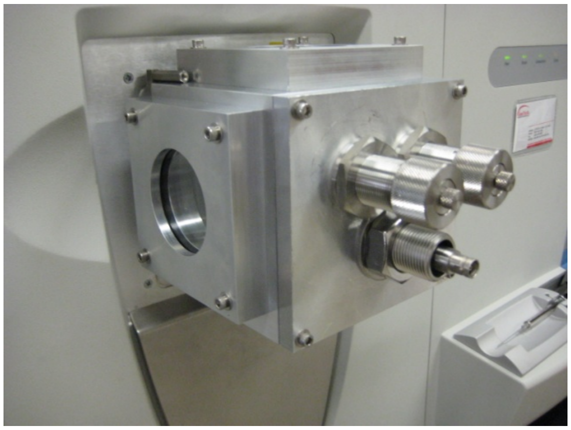

Figure 10. Environmental chamber to house new FIDI source (shown attached to Thermo Fisher LTQ-XL ion trap mass spectrometer. This allows for a controlled atmosphere around the suspended droplet, permits the use of hazardous reactants such as NOx and SO2, and avoids contamination from trace species present in laboratory air.

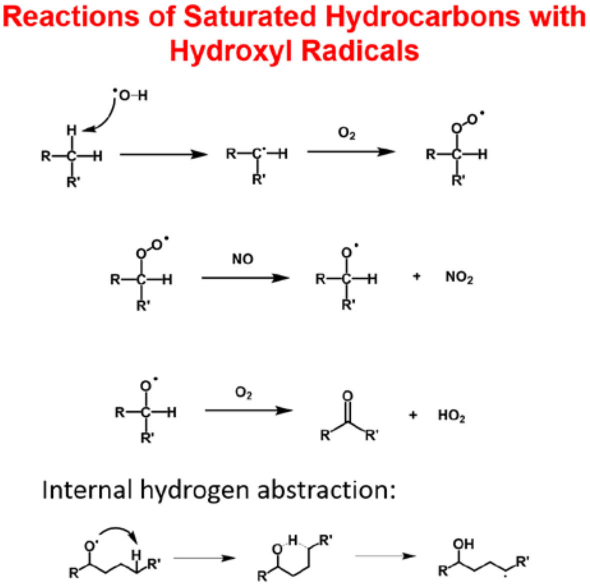

Figure 11. Primary steps in hydrocarbon oxidation initiated by hydroxyl radical. Hydrogen abstraction is followed by rapid attachment of molecular oxygen to the radical site. Subsequent reaction with NO produces an alkoxy radical which either reacts with oxygen to give a carbonyl group or undergoes internal hydrogen abstraction to form a new reactive radical site in the hydrocarbon moiety.

Because of the importance of OH radicals as a key oxidant involved in environmental chemistry, we are extending our studies of ozone reactions to include this species. Kevin Barraza in our group has initiated studies of the reactions of OH radicals with organic molecules at air-water interfaces. He has generated OH radicals by vapor phase photolysis of hydrogen peroxide and with a novel

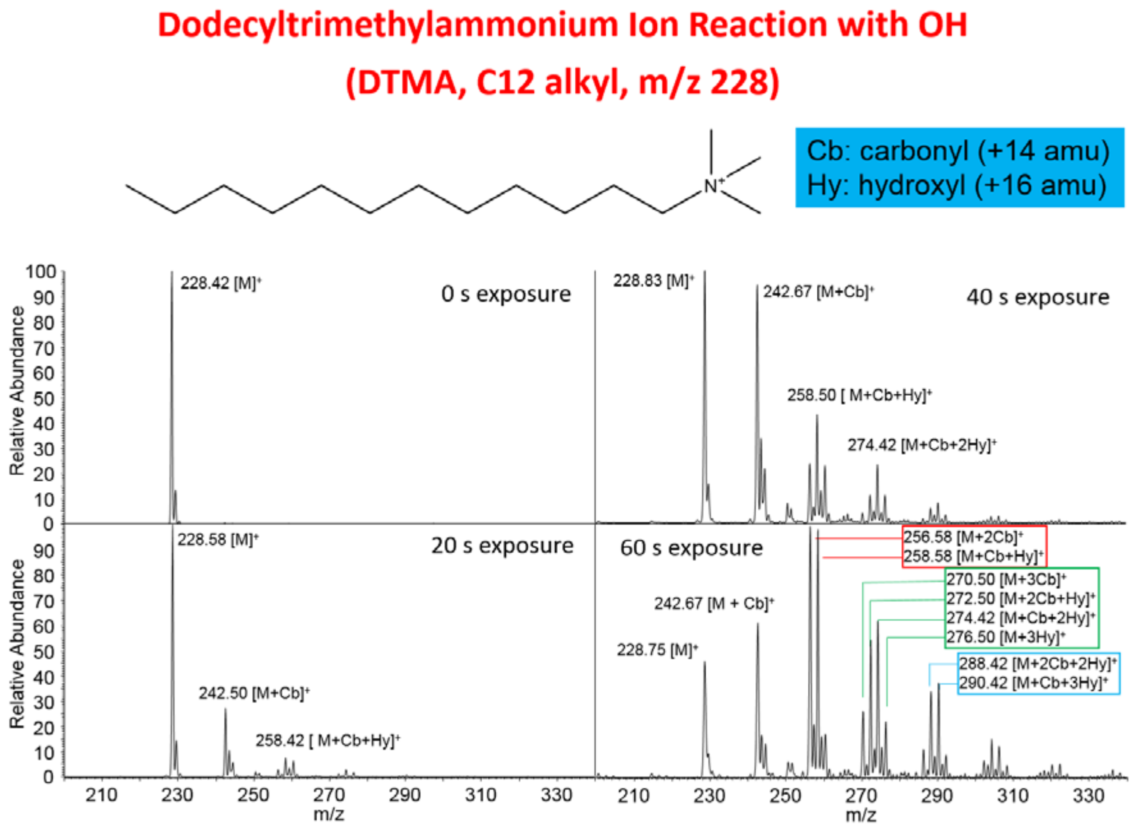

Figure 12. Oxidation products observed from reaction of OH radicals with dodecyltrimethylammonium ion at the air-water interface of a 1 mm drop for 20 sec. The rate limiting step becomes the initial oxidation (forming either a carbon oxygen double bond, adding 14 amu, or a hydroxyl group, adding 16 amu). Subsequent oxidation at this site is rapid in comparison to the remaining unreacted hydrocarbon chains. At 20 sec several steps of oxidation are already evident, even though only a few percent at most of the surfactant layer has been oxidized.

surface barrier discharge source using an argon/water gas mixture operated at atmospheric pressure. With the latter approach OH radicals are produced in sufficient yield to completely oxidize an oleic acid surfactant layer at the air water interface in 30 seconds. What we find of particular interest are the reactions (much slower) with a surfactant presenting saturated hydrocarbon chains at the air water interface. The rate limiting step becomes the initial oxidation (forming either a carbon oxygen double bond, adding 14 amu, or a hydroxyl group, adding 16 amu). The main reactions occurring are illustrated in Figure 11. Subsequent oxidation adding multiple oxygens is rapid in comparison to the remaining unreacted hydrocarbon chains. This is illustrated in Figure 12 for the reaction of OH with dodecyltrimethylammonium ion to mimic hydrocarbons at an air-water interface. Use of ^{18}OH labeled radicals will facilitate studies of the complex mechanisms of these reactions.

In summary, we have developed novel experimental methodology to facilitate the study of complex chemical reactions of environmental interest at air-water interfaces. There are many opportunities for students interested in a SURF project to become involved with these studies. Contact Professor Beauchamp if you would like to discuss this possibility (jlbchamp@caltech.edu).

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