

Supplementary information for

Experimental Evidence that Halogen Bonding Catalyzes the Heterogeneous Chlorination of Alkenes in Submicron Liquid Droplets

*Meirong Zeng and Kevin R. Wilson**

Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA.

Corresponding Author*: Kevin R. Wilson (email: krwilson@lbl.gov)

S1. Temperature dependence of the uptake coefficient using a simplified resistor model

Here we use a resistor model of trace gas uptake^{1,2} to estimate the temperature dependence of γ for the limiting case where uptake is controlled only by Cl₂ solubility, diffusion and reaction. In the absence of surface processes, the reactive uptake coefficient (γ),

$$\gamma \sim \frac{4HRT}{\bar{c}} \sqrt{Dk[\textit{alkene}]} \quad (\text{Eq. S1})$$

depends on the mean speed (\bar{c}) of gas phase Cl₂, the Henry's law constant (H) and diffusion constant (D) for Cl₂ in Sqe. k is the bimolecular rate coefficient for Cl₂ + Sqe reaction. H, D, and k depend upon temperature. To our knowledge, the temperature dependent solubility of Cl₂ in squalene has not been measured, so instead it is approximated by the temperature dependence of H for Cl₂ in decane.³ As shown in Fig. S1A, H_{cc} (dimensionless Henry's law constant) increases by $\sim 3\times$ with decreasing temperature over the range used in our experiments. Similarly, we are unable to find the temperature dependence of D for Cl₂ in squalene in prior literature. Instead, we estimate this from the temperature dependence of D for Cl₂ in water,⁴ as shown in Fig. S1B. As expected D increases with increasing temperature. To estimate the temperature dependence of k

(Fig. S1C), we use the data reported by Yates and Leung⁵ for the Cl₂ + styrene reaction. As expected for a reaction with a barrier, the rate coefficient increases with temperature.

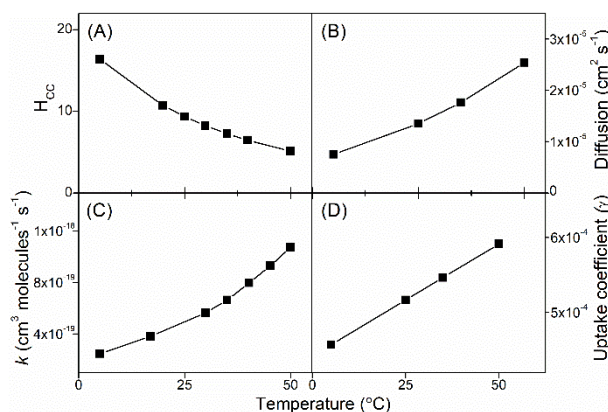


Figure S1. (A) The dimensionless Henry's law constant (H_{cc}) of Cl₂ in decane and (B) the diffusion constant of Cl₂ in water as a function of temperature. (C) The temperature dependence of the bimolecular rate constant (k) the reaction of Cl₂ with styrene. (D) The calculated uptake coefficient vs. temperature using Eq. S1.

Together the temperature dependences for H , D and k are used to estimate how γ is expected to vary with temperature using Eq. S1. Although H increases with decreasing temperature, favoring a larger γ at lower temperatures, this contribution to γ is outweighed by the opposite temperature dependence of D and k . Thus, γ is estimated to actually decrease as temperature is lowered. Even if the temperature dependence of D for Cl₂ in squalene is much weaker than in H₂O (the most uncertain portion of this estimate), we would nevertheless expect that γ remains nearly invariant with temperature or slightly increasing with decreasing temperature. This estimated temperature trend is opposite of what is observed in the experiment (Fig. 6), which suggests that the increase in γ with decreasing temperature originates from temperature dependence of surface processes (e.g. the Cl₂ desorption kinetics), which are not explicitly considered in Eq. S1.

S2. Supplementary information for the neat LA (or OA) experiments

Figure S2 shows the detected reaction products (LA-2 and LACl) and corresponding reaction scheme for the chlorination of neat linoleic acid (LA). The reaction proceeds via the electrophilic addition of Cl₂ to the C=C bond to produce LACl_n. These chlorinated products are detected as ion fragments due to dissociative photoionization, which eliminates one or more HCl.

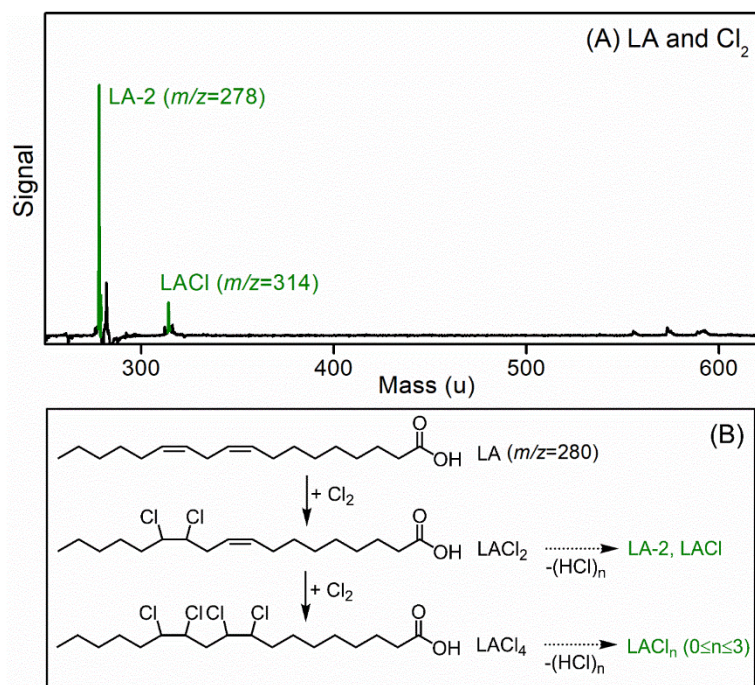


Figure S2. (A) Difference mass spectra (reacted – unreacted LA) showing the reaction products (LA-2 and LACl) for the LA + Cl₂ reaction. (B) Reaction scheme for forming LACl₂ and LACl₄, which are detected at *m/z*'s corresponding to LA-2 and LACl after dissociative photoionization and HCl elimination.

Figure S3 shows the sole detected reaction product (OA-2) and its formation pathway in the neat oleic acid (OA) experiment. A single C=C bond in OA produces only one reaction generation, namely OACl₂, which is detected, due to fragmentation, as OA-2 as shown in Fig. S3B.

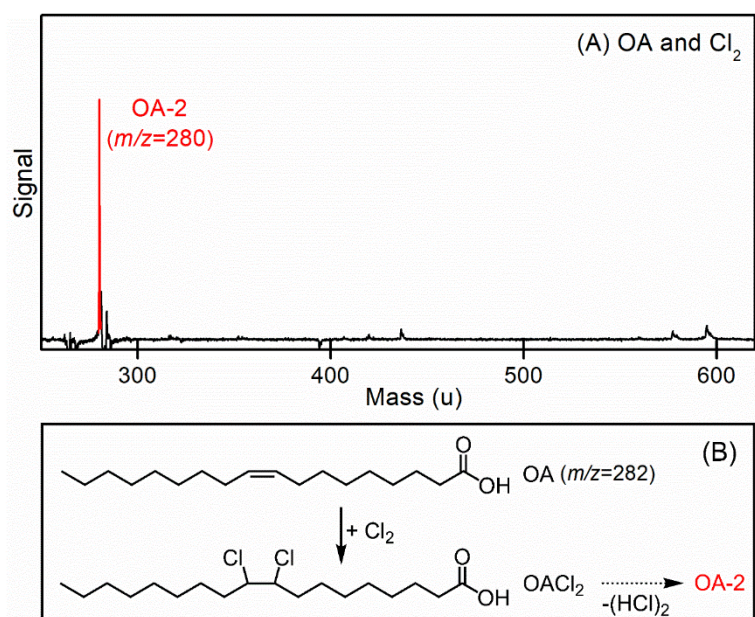


Figure S3. (A) Difference mass spectra (reacted – unreacted OA) showing a single reaction product (OA-2). (B) Reaction scheme for forming OACl₂, which is detected at a *m/z* corresponding to OA-2 after dissociative photoionization and –HCl elimination.

The effective uptake coefficients for the reaction of Cl₂ with neat LA and OA are of similar magnitude to, or even slightly smaller, than that of neat Sqe, *e.g.* $\gamma_{eff}^{LA} = 2.9 \times 10^{-5} < \gamma_{eff}^{Sqe} = 3.5 \times 10^{-5}$. The similarity of γ_{eff}^{LA} and γ_{eff}^{Sqe} suggests that the –COOH group in pure LA (or OA) aerosol does not appreciably accelerate the decay of LA (or OA), which is different from the observed rate acceleration observed when LA or OA is mixed with Sqe. This difference could arise from differences in molecular ordering in pure LA or OA vs. in liquid mixtures with Sqe. For example, in neat OA,⁶⁻⁸ there is a significant population of dimers present, which are formed by hydrogen-bonding between neighboring –COOH groups. In mixtures with Sqe, however, due to dilution, the dimer populations are expected to be substantially diminished. This is supported by evidence in Refs.,^{7, 8} which find that the introduction of additives shifts the population of OA dimers to monomers. For example, in the presence of cholesterol,⁷ OA dimers are disrupted and instead form hydrogen-bonds to the –OH group of cholesterol. Thus it seems reasonable to conclude that in Sqe/OA mixtures, the –COOH groups are more readily available for halogen bonding to Cl₂, whereas in the neat OA liquid there will be a competition between halogen bonding to chlorine and intermolecular hydrogen bonding between OA molecules.

S3. Supplementary information for the Sqe/LA mixture experiments

Figure S4 shows two measurements that are experimental checks. In the first experiment Sqe and LA are mixed together into the same aerosol. As shown in Fig S4A, when in an internal mixture the decay kinetics of Sqe are substantially accelerated relative to LA. In the second experiment, Sqe and LA are produced in separate aerosol populations (*i.e.* an external mixture). In this case, (Fig. S4B) the Sqe decay is much slower than in Fig. S4A and similar to LA. This experimental check confirms that LA molecules significantly accelerate the chlorination of Sqe only when they reside in the same aerosol. This experimental check also eliminates the possibility that gas-phase reaction products (invisible to our aerosol mass spectrometer) arising from the chlorination of LA are somehow responsible for the accelerating the kinetics of Sqe shown in Fig. S4A.

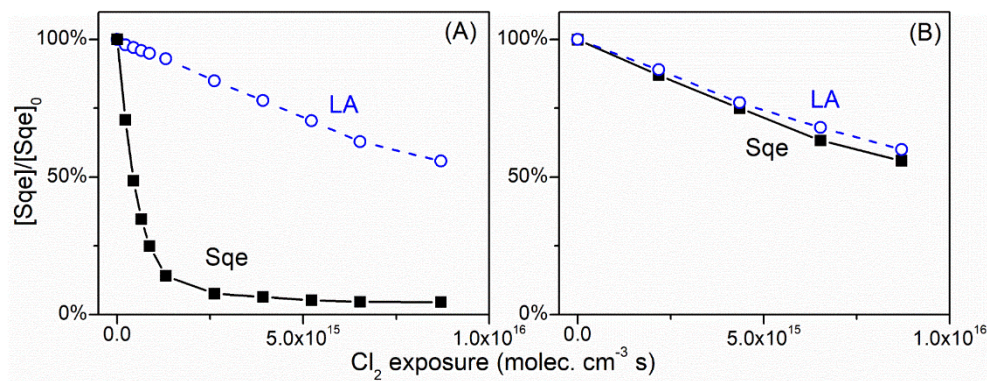


Figure S4. Normalized decay of Sqe and LA as a function of chlorine exposure for: (A) binary Sqe/LA aerosols (*i.e.* Sqe and LA are in same particles) and (B) Sqe and LA aerosols produced by two different two ovens (*i.e.* Sqe and LA are in different particles).

Figure S5 shows γ_{eff} computed for Sqe and LA in the Sqe/LA mixture experiments. This is done by separately monitoring the decay of peaks in the mass spectrum corresponding to Sqe and LA. γ_{eff}^{Sqe} is observed to increase with increasing mole fraction of LA, whereas γ_{eff}^{LA} decreases. These opposing trends highlight the kinetic competition between chlorinating Sqe and LA. At small LA fractions, Sqe (containing six C=C bonds) is more reactive towards Cl_2 compared to LA portion with only two C=C bonds).

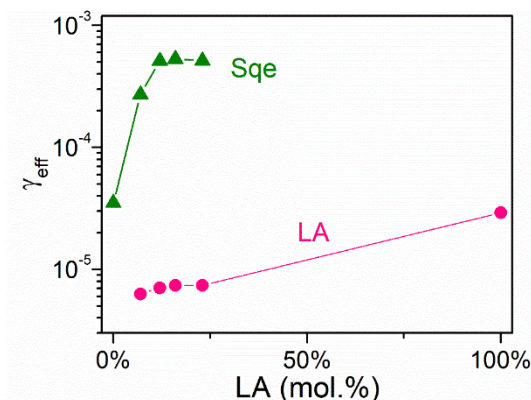


Figure S5. γ_{eff} for Sqe and LA as a function of LA mole fraction for binary aerosol mixtures of Sqe and LA. Symbols are experiments, which are connected by solid lines to guide the eye.

S4. Supplementary information for Sqe and BES (/Sqa) mixture experiments

Figure S6 shows the reaction products that form in Sqe/BES and Sqe/Sqa mixtures. These products are similar, if not identical, to those observed during chlorination of neat Sqe aerosol (Fig. 1). This is expected since both BES and Sqa lack reactive C=C moieties for chlorination.

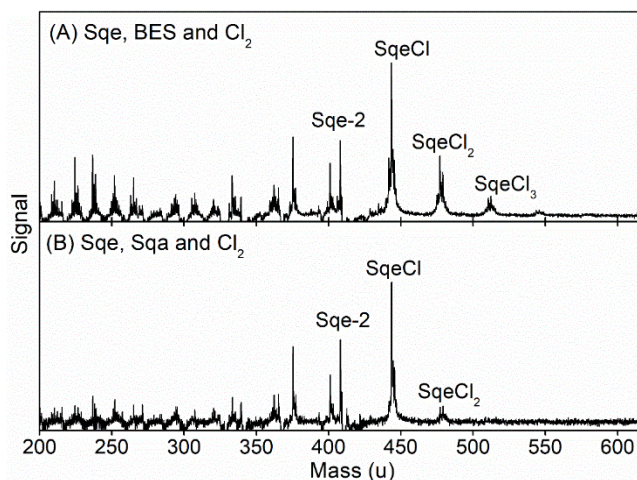


Figure S6. Difference mass spectra (reacted – unreacted Sqn) showing a series of SqnCl_n reaction products in: (A) Sqn/BES and (B) Sqn/Sqa mixture experiments.

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