Dynamics of interfacial collisions of OH with organic liquid surfaces

Kerry L. King, [1] Grant Paterson, [1] Matthew L. Costen[1] and Kenneth G. McKendrick[1,*]

[1] Heriot-Watt University, Edinburgh, EH14 4AS.
* Corresponding author: Kenneth.G.McKendrick@hw.ac.uk

T
U
E
S
D
A
Y

The dynamics of potentially reactive gas-liquid interfacial collisions remain relatively unexplored, but are of intrinsic fundamental interest. They are also of widespread applied importance, for example in heterogeneous atmospheric chemistry. We present an experimental investigation of the dynamics of gas-liquid interfacial collisions of OH radicals with organic liquids chosen partly for their interest as mimics of the surfaces of atmospheric aerosols.

The OH radicals were produced by photolysis of a gas-phase precursor. Those that survive and recoil from the continually refreshed liquid surface are intercepted by a tunable probe laser beam which excites laser-induced fluorescence (LIF) on the OH A-X band.

Two different precursors were used to enable a range of translational and internal OH energy distributions to be prepared. More recent measurements used photolysis of allyl alcohol at 193 nm, generating OH that is both translationally ($<E_T> \sim$ 85 kJ mol^{-1}) and rotationally ($T_{rot} \sim$ 2000 K in both v = 0 and 1) excited. This complements previous work based on photolysis of HONO at 355 nm, resulting in translationally hot ($<E_T> \sim$ 54 kJ mol^{-1}) but rotationally colder (close to thermal) OH.[1,2] We have characterized the collisions of both these distributions with the surfaces of a series of liquids, including an inert reference, PFPE (perfluoropolyether), and representative long-chain, partially branched saturated and unsaturated hydrocarbons. Two distinct types of measurements have been made. The first is the appearance profile for a particular scattered product level as a function of photolysis-probe delay. This contains information on the internal state-specific translational energy distribution. The second is the LIF excitation spectrum at a fixed delay, revealing the internal product-state distribution for a velocity subgroup. Contributions from molecules that have not collided with the surface are removed by subtraction of the corresponding data with no liquid surface present.

We find strong and unambiguous positive correlations between product rotation and translation in the scattered OH v' = 0 products for all the liquids examined. This is particularly clear for the rotationally hotter OH from allyl alcohol. Overall, this OH experiences a significant net rotational cooling. In contrast, for HONO, the dominant scattering process is T→R transfer, with a gain in rotational energy at all the surfaces.[2] There are clear differences in the inelastic scattering from different liquids, with, as expected, PFPE presenting a 'harder' surface than the hydrocarbons. These observations can be interpreted in terms of a combination of direct, ballistic scattering, and indirect thermal desorption. The reactive uptake can also be inferred from comparison of the OH yield from PFPE with that from the other liquids. OH is lost at both saturated and unsaturated hydrocarbon surfaces. A very interesting subtlety is that although the survival probability of the directly scattered OH is similar in both cases, it is distinctly lower for rotationally and translationally cold OH from unsaturated surfaces. This is consistent with an additional reactive loss channel due to capture of thermalised OH at the double-bond sites.

1.   P. A. J. Bagot, C. Waring, M. L. Costen and K. G. McKendrick, *J. Phys. Chem. C*, 2008, **112**, 10868-10877.
2.   C. Waring, K. L. King, P. A. J. Bagot, M. L. Costen and K. G. McKendrick, *Phys. Chem. Chem. Phys.*, 2011, **13**, 8457-8469.