Title: Dynamics of interfacial reactions between O(3P) atoms and long-chain liquid hydrocarbons

Short title: Gas-liquid interfacial reactions: O(3P) + hydrocarbons

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Abstract

Recent progress that has been made towards understanding the dynamics of collisions at the gas-liquid interface is summarised briefly. We describe in this context a promising new approach to the experimental study of gas-liquid interfacial reactions that we have introduced. This is based on laser-photolytic production of reactive gas-phase atoms above the liquid surface and laser-spectroscopic probing of the resulting nascent products. This technique is illustrated for reaction of O(\(^3\)P) atoms at the surface of the long-chain liquid hydrocarbon squalane (2,6,10,15,19,23-hexamethyltetracosane). Laser-induced fluorescence detection of the nascent OH has revealed mechanistically diagnostic correlations between its internal and translational energy distributions. Vibrationally excited OH molecules are able to escape the surface. At least two contributions to the product rotational distributions are identified, confirming and extending previous hypotheses of the participation of both direct and trapping-desorption mechanisms. We speculate briefly on future experimental and theoretical developments that might be necessary to address the many currently unanswered mechanistic questions for this, and other, classes of gas-liquid interfacial reaction.
1. Introduction

1.1 General motivation

The gas-liquid interface is a central element of many important phenomena. These include natural processes, ranging from biological respiration to the processing of atmospheric constituents on aerosol droplet surfaces, and man-made activities such as distillation, combustion of liquid fuels and oxidation of lubricants.

Despite this importance, the current molecular-level understanding of the dynamics of interactions at the gas-liquid interface is very underdeveloped compared to the corresponding processes in the homogeneous gas-phase, or even the gas-solid interface. In this article we review briefly the previous progress that has been made, much of it relevant recently, that has begun to change this situation. In particular, we describe in the context of previous work a new approach to the experimental study of gas-liquid interfacial reactions that we have introduced. We present some of the key results and the mechanistic conclusions inferred from them. We speculate briefly on the future developments that might be necessary to address some currently unanswered mechanistic questions.

1.2 Previous work

1.2.1 General gas-liquid interfacial kinetics

There is a reasonably well-developed literature on the measurement of bulk kinetics of reactions at the gas-liquid interface, primarily motivated by the important role that aerosols are now known to play in atmospheric chemistry. The reactive species which have been investigated therefore tend to be those of atmospheric interest, including atoms, small free radicals and reactive molecular species such as ozone. A variety of mimics have been used as proxies for the aerosol surface,
including bulk liquids,\textsuperscript{7} frozen liquid surfaces,\textsuperscript{8} droplet trains \textsuperscript{9, 10} and more ordered surfaces such as self-assembled monolayers (SAMs).\textsuperscript{3, 6, 11, 12, 13} Many of the surfaces selected have been organic, for the reason that the hydrophobic organic components of aerosols are known to accumulate at their outer surfaces.\textsuperscript{14} Even trace levels of organic constituents can therefore have a substantial effect on the chemistry of the aerosols. The subsequent oxidation of the outer layers plays a crucial role, for example, in the growth rate of the aerosol through uptake of further water and therefore their effectiveness as cloud-condensation nuclei.

From a mechanistic point of view, one of the more interesting interpretations of these studies is an inferred substantial increase, of several orders of magnitude, of the gas-liquid reactivity relative to that of the corresponding reaction in the homogeneous gas phase. Specific examples include the reactions of OH and O(\textsuperscript{3}P) with saturated hydrocarbon surfaces,\textsuperscript{1, 2, 3} where the estimated enhancement over reactions with gas-phase organic molecules was of order 25 and 10\textsuperscript{3}, respectively. This currently remains a largely unexplained empirical observation, but it does point to the possibility of distinct changes in mechanism between isolated, bimolecular collisions and potentially more complex gas-liquid interfacial reactions.

\textit{1.2.2 Specific interfacial O(\textsuperscript{3}P) + hydrocarbon reactions}

The specific reaction that is the focus of our work is between gas-phase, ground state oxygen atoms, O(\textsuperscript{3}P), and long-chain liquid hydrocarbons. A particular, albeit specialised, reason for the applied interest in this class of reactions is because of the serious erosion experienced by polymeric materials on the surfaces of spacecraft in low-Earth orbit. At the typical altitudes of 200-700 km, O(\textsuperscript{3}P) is the predominant component of the atmosphere. Collisions of O(\textsuperscript{3}P) with the surface of an orbiting
spacecraft therefore have a high relative kinetic energy, of order 500 kJ mol\(^{-1}\). This has stimulated a considerable literature on the quantification and understanding of the reactions that lead to bulk erosion of material.\(^7,\,13,\,15,\,16,\,17,\,18,\,19,\,20,\,21,\,22,\,23\)

Moreover, this reaction is a good candidate for new, dynamical interfacial studies because there is a well established basis of fundamental investigations of the corresponding gas-phase reaction of O\(^{(3P)}\) with shorter chain hydrocarbons.\(^{24}\) In summary, a combination of experimental\(^{24,\,25,\,26,\,27,\,28,\,29,\,30}\) and theoretical\(^{24,\,31,\,32,\,33,\,34,\,35}\) studies has consistently indicated that the lowest-energy channel is direct hydrogen abstraction via a tightly constrained collinear geometry.

1.2.3 Previous dynamical studies of gas-liquid interfacial scattering

The majority of what is now known about dynamics at the gas-liquid interface has been deduced from studies of inelastic scattering. The predominant experimental technique has been based on the use of molecular beams, yielding well-resolved velocity (speed and angular) distributions of the scattered species. Essentially all experimental approaches so far devised are practically constrained to use low vapour pressure liquids. These include liquid metals, or molecular liquids that are either heavily hydrogen-bonded, such as glycerol or sulphuric acid, or of high molecular weight, such as the long-chain hydrocarbons of interest in our work. Typical examples of the inelastically scattered species include rare gases such as Ne, Ar and Xe\(^{36}\) along with small stable molecules such as NH\(_3\) and CH\(_4\).\(^{37}\)

Much less common has been the use of complementary spectroscopic methods to probe the internal states of the inelastically scattered molecules. An early, original study of this type was of molecular iodine on liquid Ga and methylated poly-siloxane oil surfaces,\(^{38}\) with detection of the inelastically scattered I\(_2\) by laser-induced
fluorescence (LIF). More recently, high-resolution IR-laser absorption has been used to investigate the scattering of CO₂ from perfluoroether surfaces.³⁹

A recurrent theme in the mechanistic interpretation of the inelastic scattering experiments is the existence of at least two components in the speed and angular distributions. The first corresponds to molecules that have rebounded essentially “directly”, transferring momentum to the surface in a ballistic fashion. The second consists of those that have been “trapped” for a finite period, and in the limit of a sufficient number of secondary encounters have become fully thermally accommodated at the surface temperature, before subsequent thermal desorption. The direct component has not only higher speeds but also tighter angular distributions centred near the specular angle. The trapping-desorption component has speeds approximating to a Maxwell-Boltzmann distribution at the surface temperature, described by a cosθ distribution about the surface normal. The extent to which intermediate scattering mechanisms that depart from these limiting cases might also be distinguishable is a matter of active debate.

The number of studies of reactive scattering at the gas-liquid interface is considerably more limited. The first steps taken in this direction were a natural extension of the molecular beam methods developed for inelastic scattering, for example in the exchange processes that take place in HCl/ DCl + sulphuric acid collisions.⁴⁰, ⁴¹ A key forerunner to our own studies of the O(³P) + hydrocarbon system was the molecular beam investigations of O(³P) with squalane (2,6,10,15,19,23-hexamethyltetracosane).⁷, ¹⁷, ⁴², ⁴³, ⁴⁴ Squalane is readily commercially available and has an ideal combination of low vapour pressure (<10⁻⁸ mbar) over a wide range of temperatures above a relatively low melting point (235K). The O(³P) source in the early phases of this work was a conventional continuous discharge, which was
subsequently replaced by a pulsed CO$_2$-laser detonation beam source capable of reproducing the very high energies relevant to the low-Earth orbit environment introduced above.

The main conclusions from these molecular beam scattering studies of O($^3$P) with squalane were that three species, inelastically scattered O($^3$P) and nascent reactive products OH and H$_2$O, were detected. The branching between these channels was not estimated quantitatively. Very interestingly, they all showed characteristics of the bimodal speed and angular distributions seen previously for inelastically scattered products, taken to imply a similar kind of multi-component mechanism.

It was in this context that we first introduced$^{45}$ our alternative, spectroscopically based approach to the detection of the OH product of the O($^3$P) + squalane reaction. This was the first time that internal state distribution of a reactive product of any gas-liquid interfacial process had been detected. They complemented, for this particular reaction, the existing velocity distributions in the molecular beam experiments of Minton and co-workers.$^7, 42, 43, 44$ We describe our method in more detail below, together with our principal mechanistic conclusions$^{46, 47}$ before concluding with a broader view of prospects for future experimental and theoretical developments in this field.

2. Experimental approach

The basis of our experimental approach is outlined in figure 1. Further details are given elsewhere.$^{45-47}$ In essence, reaction is initiated by laser photolysis of a low pressure of a suitable precursor, in this case NO$_2$, a short distance above the liquid surface. As far as we are aware, this method, which has seen widespread use for the study of gas-phase bimolecular reactions, has not been exploited elsewhere in the
context of gas-liquid scattering. It relies on the fact that for a typical viable precursor pressure of 1 mTorr, the mean free path is of order 5 cm, compared to typical practical laser beam-surface distances of 5 mm. Therefore the products escaping from the surface, which are detected by the counter-propagating probe laser pulse, are “nascent” in the sense that they have a low probability of having suffered any secondary collisions in the gas phase.

We ensure that the surface of the liquid is continuously refreshed using a rotating stainless-steel wheel device of a similar design to those introduced by others.\textsuperscript{48, 49, 50} The wheel is immersed in a copper bath filled with liquid squalane or other hydrocarbon. It rotates past a Teflon® spacer, producing an even film of liquid over its surface. The temperature of the bath is controlled using a Peltier element, and can be varied over a current operational range of approximately 263 K to 353 K. The whole liquid surface apparatus is contained within a custom-built stainless-steel reaction chamber, with entrance and exit arms for the laser beams.

We use commercial pulsed lasers for the initiation and detection steps. Photolysis of NO$_2$ is induced by the 355 nm third harmonic of a Nd:YAG laser with a ~5 ns pulse length. This produces a relatively broad O($^3$P) speed distribution, with an average laboratory-frame collision energy of 15.8 kJ mol$^{-1}$ and a full width at half maximum of around 26 kJ mol$^{-1}$. We therefore do not approach the “hyperthermal” energy regime of low-Earth orbit, but there is still sufficient collision energy for a fraction of the O($^3$P) atoms to overcome the typical 20-40 kJ mol$^{-1}$ barriers for hydrogen atom abstraction\textsuperscript{24} from the hydrocarbon liquid. The probe laser is a Nd:YAG-laser pumped tunable dye laser with a similar ~5 ns pulse length. This excites laser-induced fluorescence (LIF) from the escaping OH radicals on the well-characterized A-X band. Fluorescence is collected perpendicular to the laser beams, suitably isolated
using custom interference filters, and detected by a photomultiplier tube. The signals are then captured electronically and processed in the usual way on a dedicated laboratory computer.

![Schematic diagram of experimental setup](image)

**Figure 1.** Schematic outline of the experimental approach. The photolysis and probe lasers counter-propagate into and out of the plane of the page, respectively.

### 3. Supporting Molecular Dynamics calculations

To complement our experimental approach, and in particular to provide some insight into the structure of the liquid surface to aid mechanistic conclusions to be drawn, we have undertaken a parallel programme of molecular dynamics simulations.\(^{51}\) We do not attempt to describe the details here, but in essence a large sample (typically many hundred) of squalane, or other hydrocarbon, molecules are confined to a 3-dimensional box with periodic boundary conditions in all three dimensions.\(^{51}\) The molecules form a condensed “slab”, which is considerably thinner than the longest
The dimension of the box, so that two gas-liquid interfaces are formed. The system is allowed to relax at a given temperature under the influence of a suitable force field, available from previous independent work, such as Siepmann’s United Atom model.\textsuperscript{52} Once equilibrium has been established, statistical properties of the interfaces are analysed over a trajectory of typically several nanoseconds produced by the MD simulations.\textsuperscript{51} A typical “snapshot” of the squalane surface is shown in Fig. 2. In broad terms, the most significant structural feature is the atomically rough, open nature of the surface, with all three atom types (primary, secondary and tertiary C-H units) all clearly exposed to an incoming projectile.

Figure 2. View from above of an MD-simulated liquid squalane surface at 298 K. The different C-H atom types are indicated by colour coding: (blue) primary; (red) secondary; (green) tertiary. Darker and lighter atoms are C and H, respectively.

4. Key results and mechanistic conclusions
Our experimental data are essentially two dimensional; the independent variables correspond to the time delay between laser pulses and the wavelength of the probe laser. By varying the delay, we can measure a “time-of-flight” appearance profile for a given spectroscopic line and hence internal OH quantum state. An example of this type is shown in figure 3 (the additional features present are discussed further below).

Figure 3. Measured appearance profile for OH $v’=0$ (open circles) from the reaction of O($^3P$) with liquid squalane. Probe line: OH A-X (1,0) Q1(1). Laser-beam–surface distance = 5 mm. $p$(NO2) = 1 mTorr. Thick lines represent Monte Carlo simulation (direct (dotted), trapping-desorption (dashed) and their sum (solid)) contributions to the signal. Vertical lines indicate delays at which LIF excitation spectra are typically measured.
Figure 4. OH A–X (1,0) LIF excitation spectrum, recorded at the rising edge of the OH appearance profile from reaction of O(3P) with a liquid squalane surface. Liquid temperature = 343 K; \( p(\text{NO}_2) = 1\) mTorr; distance surface-probe laser ~ 5 mm; photolysis-probe delay = 6 µs.

Alternatively, we can fix the delay between the lasers and measure a LIF excitation spectrum. This yields (following a suitable normalisation procedure\(^{45}\)) the OH internal state distribution for, loosely speaking, a given OH product velocity. A typical example spectrum is shown in figure 4. Both classes of measurement can be repeated as a function of the other experimental parameters. The most significant of these are the identity of the liquid and its temperature. For operational reasons it is also sometimes desirable to vary other parameters such as the laser beam-surface distance, but in principle this does not reveal any fundamentally new information.
At the most basic level, the presence in Fig. 3 of the initial “induction period”, during which no OH is observed, confirms that the signal authentically results from reaction at the surface. Reassuringly, the length of this period and the magnitude of the signal both scale sensibly with variations in the laser beam to surface distance.\textsuperscript{46} We had also independently confirmed that the products must be formed at the surface in our earliest measurements\textsuperscript{45} by using a deuterated sample of squalane.

The additional curves in Fig. 3 are the results of Monte Carlo simulations of the predicted appearance profiles for direct and trapping desorption contributions to the signal. Details of the model are described elsewhere.\textsuperscript{46} It takes account of the known O(\(^{3}\)P) velocity distributions and geometric averaging effects in our experiments. It is necessary to appeal in part to the results of the much better-resolved velocity measurements in the molecular-beam experiments of Minton’s group, in particular to define an effective mass for the fragment of the squalane molecule with which the directly scattered OH recoils and its angular distribution.\textsuperscript{7}

Even a most conservative interpretation of our appearance profiles acknowledges that they cannot be explained without including a “direct” component that is substantially faster than would be observed from thermal desorption. In this respect we confirm the previous molecular beam data\textsuperscript{7, 17, 42, 43}. The entirely new results that we obtain come from the analysis of the LIF excitation spectra, such as in Fig. 4, and their correlation with the point in the appearance profile at which they are measured. A major notable observation is that vibrationally excited molecules are able to survive and escape the surface, with both OH \(v'=0\) and 1 produced in significant yield. Our estimate\textsuperscript{46} for the OH (\(v'=1\)) / (\(v'=0\)) branching fraction is 0.07 ± 0.02 for squalane at the peak of its appearance profile at 298 K. This increases, for understandable straightforward energetic reasons, to 0.30 ± 0.10 for OD from the fully deuterated isotopomer. We
interpret this, by analogy with the known vibrational branching ratios in the corresponding gas-phase reactions with shorter-chain hydrocarbons\textsuperscript{24} and consistent with established general principles, as evidence that the \( \text{O} (^2\text{P}) \) atoms must be capable of accessing the weaker secondary and tertiary C-H bonds along the squalane backbone. This is reinforced by the prediction of our MD simulations.\textsuperscript{51} We do find a slight preference for methyl groups to dominate the outermost layers of the surface, as had been suggested previously\textsuperscript{53} for linear hydrocarbons. However, this is insufficient to bias the chances of an incoming atom encountering and reacting with a more or less statistical distribution of the different C-H bond types in the squalane molecule.

More subtly, we have measured the rotational distributions for both \( v' = 0 \) and 1 at two points in their respective appearance profiles, corresponding to the rising edge and the peak as indicated in figure 3. We find in all cases that these can be reasonably well fit by a Boltzmann distribution. Although in the case of direct scattering, at least, there is no reason in principle why they should be described exactly in this fashion, it is convenient to be able to summarize the distributions in terms of a single parameter, the effective rotational temperature, \( T_{\text{rot}} \).

The rotational temperatures derived in this way are summarized in Table 1.\textsuperscript{47} What this shows in essence is that \( T_{\text{rot}} \) is indeed sensitive to all three variables: appearance time, vibrational level and liquid surface temperature, \( T_{\text{liq}} \). Crucially, the extents to which they each exert an influence are correlated systematically. At the rising edge of the profile, \( T_{\text{rot}} \) for \( v' = 0 \) and 1 are quite distinct, with \( v' = 0 \) significantly hotter than a thermal distribution and \( v' = 1 \) slightly cooler. This qualitative variation, and indeed the absolute rotational temperatures, is highly reminiscent of the results for the corresponding homogeneous gas-phase reactions.\textsuperscript{24} In addition, at the rising edge the measured \( T_{\text{rot}} \) values from the squalane surface are essentially independent of \( T_{\text{liq}} \),
especially for $v' = 0$. Both these observations are consistent with the conclusion that these fastest moving product molecules are produced in a direct process in a single, or at least sufficiently small number of events, such that they scatter with non-thermalized translational (as was known) and also rotational (as we have now established) distributions.

In contrast, the measurements of $T_{\text{rot}}$ at the peak of the arrival profile show a different trend. There is now much less difference between $v' = 0$ and 1. The $v' = 0$ distribution has clearly cooled substantially and the value of $T_{\text{rot}}$ is also correlated with $T_{\text{liq}}$. This is consistent with a significant trapping desorption component, absent at the rising edge, now contributing at the peak. This identification of distinct rotational distributions further supports the decomposition into direct and trapping-desorption translational distributions illustrated in figure 3. It is harder to tell if the warming of $T_{\text{rot}}$ for $v' = 1$ is significant: this is in part simply arithmetical, because the initial difference between direct and thermalised temperatures is accidentally smaller, but may also more subtly reflect the reduction in recoil velocity because of total energy conservation for any direct contribution to $v' = 1$ production.
<table>
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<th>Surface Temperature/K</th>
<th>Rotational Temperature/K $v'=0$</th>
<th>Rotational Temperature/K $v'=1$</th>
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Table 1. Rotational Temperatures of nascent OH $v'=0$ and $v'=1$ from reaction of O($^3$P) with squalane, measured at the rising edge and peak of the appearance profiles.\(^{47}\)

5. Future directions and concluding remarks

The results presented above give a glimpse of an exciting new field, still very much in its infancy. On the experimental front, even for the most studied model of gas-liquid reactivity, O($^3$P) + squalane, there are still further mechanistic details to be unravelled. In on-going work,\(^{54}\) we are studying subtle aspects of the dependence of the relative yields of different OH vibrational levels, and their appearance profiles, as a function of liquid temperature. As yet, the mechanistic conclusions about the reactive sites in squalane have been inferred relatively indirectly from observed OH vibrational distributions. This could, in principle, be addressed more directly in future by site-selective isotopic substitution. Also remaining untested is the extent to which squalane, although experimentally convenient for the reasons discussed above, is representative of other hydrocarbons. We have also begun to address this question by investigating a range of other branched and linear molecules.
Thinking more broadly, the development of a method to obtain nascent product state distributions from higher vapour-pressure liquids, and in particular aqueous solutions, would clearly be a major experimental advance. Although this has not yet been achieved, a step somewhat in this direction has been taken by the use of “tethered” molecular surfaces, such as self-assembled monolayers (SAMs), in related work on inelastic scattering ⁵⁵, ⁵⁶, ⁵⁷, ⁵⁸ and ion-molecule reactivity.⁵⁹ The control of the structure that SAMs afford make them valuable models for the effects of surface order, as has already been demonstrated for inelastic scattering. This may well be pursued profitably in future reactive dynamical studies.

The range of potential gas-phase reactants is also, in principle, extremely broad. Even for hydrocarbon liquids, this could readily be extended to O(¹D), the first excited state of oxygen. It is known from gas-phase reactivity to exhibit insertion dynamics that are very distinct to the direct abstraction of the O(³P) ground state. The effects that this might have on gas-liquid interfacial reactivity are as yet unexplored. Beyond oxygen atoms, we note that the field has already evolved, with Nesbitt’s group having recently applied their alternative IR-absorption method to the detection of the nascent HF product from the related, but much more highly exothermic, F(²P) + squalane reaction.⁶⁰

In addition to experimental developments, there is a crucial role for parallel advances in theoretical treatments of gas-liquid scattering. The prospects are promising for the extension of the mixed quantum mechanical / molecular mechanical (QM/MM) methods that have been successfully implemented for inelastic and reactive collisions with model SAM surfaces.⁶¹, ⁶², ⁶³, ⁶⁴ These would complement and greatly extend the useful but ultimately limited picture of the surfaces alone, without the collision partner, derived from MD simulations. Features of the mechanistic understanding that
could be explored theoretically include the accessibility of different functional groups, the role of energy-dissipating collisions of the incoming projectile, the likelihood of surface penetration, and secondary collisions and potential capture of departing products. Realistic dynamical scattering calculations to predict observable quantities that would be sensitive to these processes are eagerly anticipated.

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References
