



## RESEARCH ARTICLE

# Reactions of Organic Ions at Ambient Surfaces in a Solvent-Free Environment

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**Abstract**

Solvent-free ion/surface chemistry is studied at atmospheric pressure, specifically pyrylium cations, are reacted at ambient surfaces with organic amines to generate pyridinium ions. The dry reagent ions were generated by electrospraying a solution of the organic salt and passing the resulting electrosprayed droplets pneumatically through a heated metal drying tube. The dry ions were then passed through an electric field in air to separate the cations from anions and direct the cations onto a gold substrate coated with an amine. This nontraditional way of manipulating polyatomic ions has provided new chemical insights, for example, the surface reaction involving dry isolated 2,4,6-triphenylpyrylium cations and condensed solid-phase ethanolamine was found to produce the expected N-substituted pyridinium product ion via a pseudobase intermediate in a regiospecific fashion. In solution however, ethanolamine was observed to react through its N-centered and O-centered nucleophilic groups to generate two isomeric products via 2H-pyran intermediates. The O-centered nucleophile reacted less rapidly to give the minor product. The surface reaction product was characterized in situ by surface enhanced Raman spectroscopy, and ex situ using mass spectrometry and H/D exchange, and found to be chemically the same as the major pyridinium solution-phase reaction product.

**Key words:** Solvent-free reactions, Atmospheric pressure mass spectrometry, Ion/surface reactions, Surface enhanced Raman spectroscopy, Ion soft landing

## Introduction

Organic thin films represent increasingly important materials. For example, there is growing interest in the use of such materials in electronics [1–3], as well as in catalysis and other applications [4, 5]. Moreover, thin films sequester atmospheric trace gases leading to their removal from the gas phase [6, 7], and they may also act as reactive media or as a source of reagents [8, 9]. Studies in this area have included reactions of interest in atmospheric science such as endogenous atmospheric reactions of species like  $N_2O_5$  at organic-coated particles [10], the reactive uptake of

OH and  $O_3$  by organic aerosols and films [11–13] and the little understood oligomerization reactions that lead to atmospheric organic polymers [14]. Here, we investigate the reactions of dry, isolated organic ions with reagents at surfaces under atmospheric pressure. We chose for examination a system in which the ambient ions (pyrylium ions) are readily formed and where they undergo a characteristic reaction with functionalized organics (amines). The general goal of the study is to gain insights into the differences between reactions of organic ions on organic-coated surfaces at atmospheric pressure and the corresponding reactions occurring under bulk solution-phase conditions. This was motivated by the fact that distinctive chemical reactions are often observed within an organic layer at an interface with an aqueous phase compared to the reactivity of the same compounds under bulk solution-phase conditions [15, 16].

Electrospray ionization (ESI) [17] offers a simple way to generate organic ions/aerosols in ambient air and subse-

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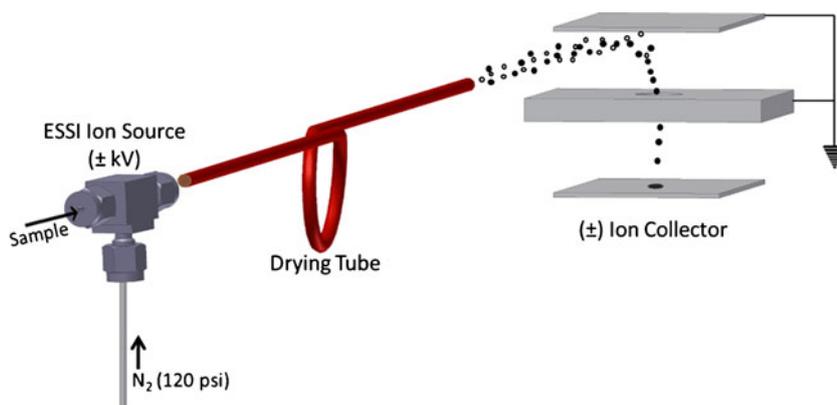


Figure 1. Experimental apparatus

well with Raman/SERS spectra recorded for other pyridinium ions [39], both from solution and solid phase. Although this phenomenon (the absence of the  $950\text{ cm}^{-1}$  band in pyridinium cations) is not well understood, the Raman/SERS spectrum of pyridine always showed the two ring breathing bands ( $\sim 992$  and  $1030\text{ cm}^{-1}$ ) [39, 40], whereas the corresponding N-substituted pyridinium species, at low concentrations, showed only one band at about  $1025\text{ cm}^{-1}$  [39]. Another notable difference between the reactant (pyrylium cation) and the product (pyridinium cation) is the width of the peak centered at  $\sim 1390\text{ cm}^{-1}$ , which is due to the unresolved  $\text{CH}_2$  wagging (alkyl chain) and C-H bending (phenyl ring) bands. It should be mentioned that the spectrum corresponding to the surface product was recorded some distance away from the landed ion spot as excess reactant may be present at the centre of the spot. (Figure S1, Supporting Information provides further information on how the reactants and products are localized on the collection surface).

The SERS results indicate that the surface reaction conditions yielded the expected reaction product (pyridinium

cation), and that unreacted pyrylium cation is not detectable at the point where the SERS spectrum was recorded. The data also indicate excess ethanolamine in the solution-phase spectrum as shown by the presence of the peak at  $1245\text{ cm}^{-1}$ . Unfortunately, information regarding the reaction mechanism could not be inferred from the SERS data. Mass spectrometry (MS) was therefore employed to understand how the unique reaction conditions present at the surface could yield the same product as the corresponding solution-phase reaction. It was expected that by using MS the presence of low abundance isomers and reaction intermediates might be detected in addition to the main reaction products. The cation landing protocol was the same as described previously [29]. After 1 h of cation landing at atmospheric pressure, the surface reaction products were washed and analyzed under vacuum using a linear ion trap instrument with tandem MS capabilities ( $\text{MS}^n$ ).

Figure 3 compares the mass spectra obtained for the surface reaction product to that of solution-phase reaction product (spectrum recorded  $<1$  min after mixing the reagents). Unlike the SERS data, the two mass spectra differ substan-

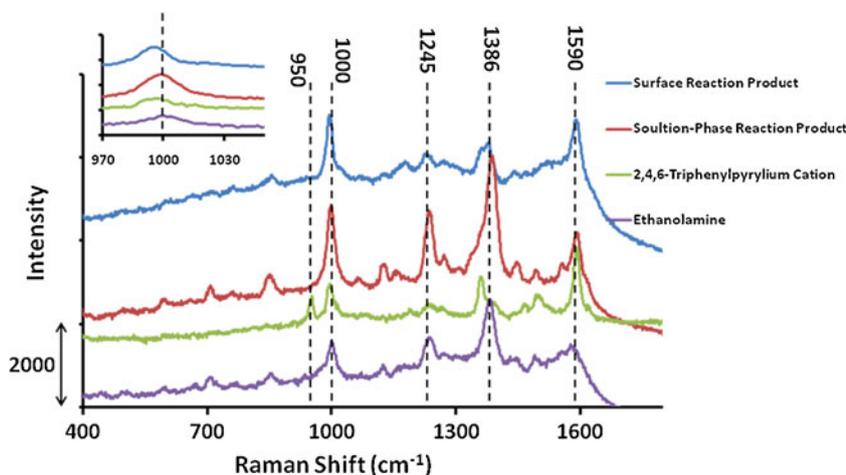
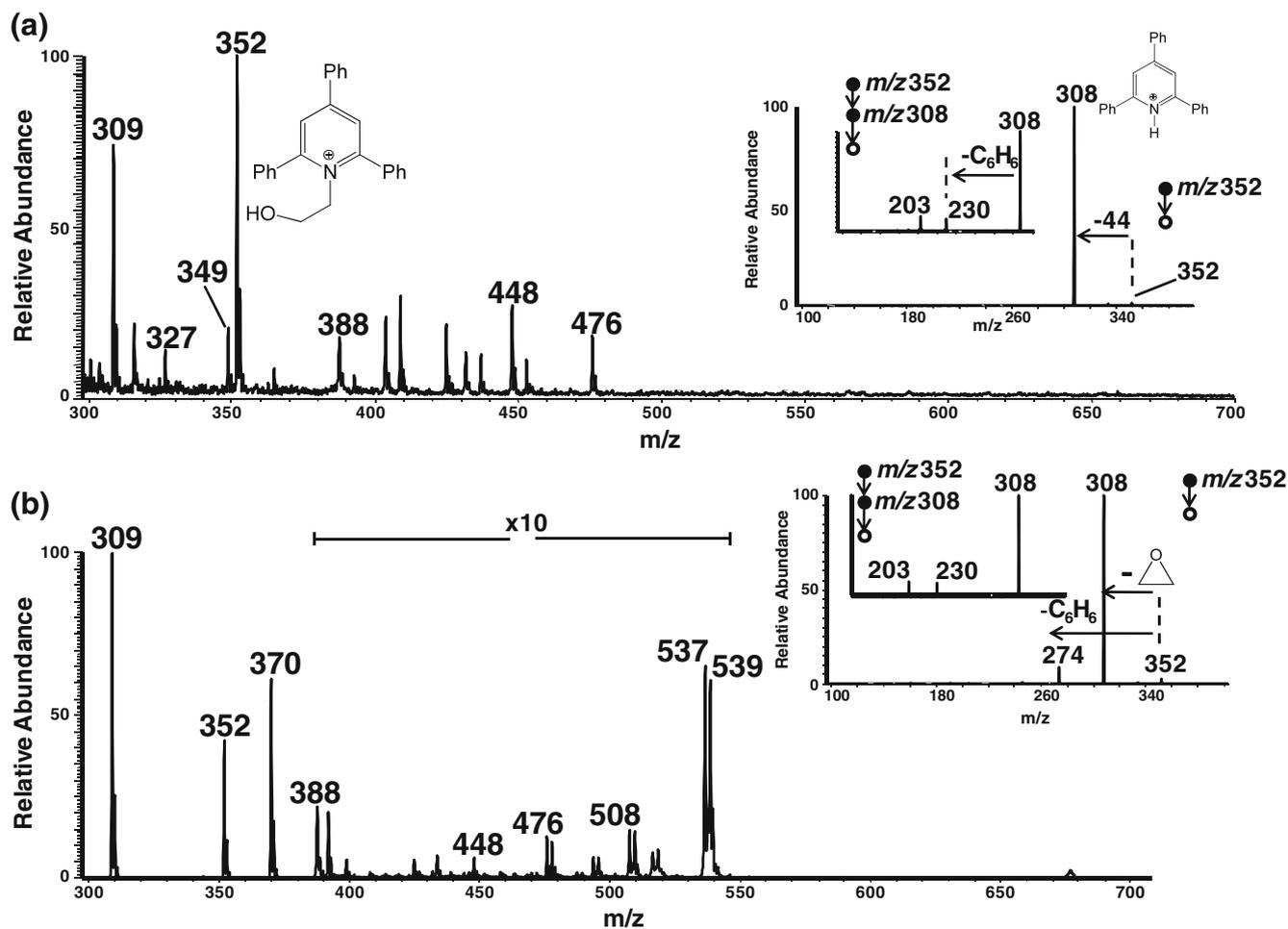


Figure 2. SERS spectra comparing reagents (ethanolamine and 2,4,6-triphenylpyrylium cation) and their reaction products, both in bulk solution phase and on the surface, in a solvent-free environment. No related features were found in Au-citrate nanoparticle blank (Figure S2, Supporting Information). Insert shows ethanolamine peak (ca  $1000\text{ cm}^{-1}$ ) relative to that due to the pyrylium cation at  $\sim 995\text{ cm}^{-1}$

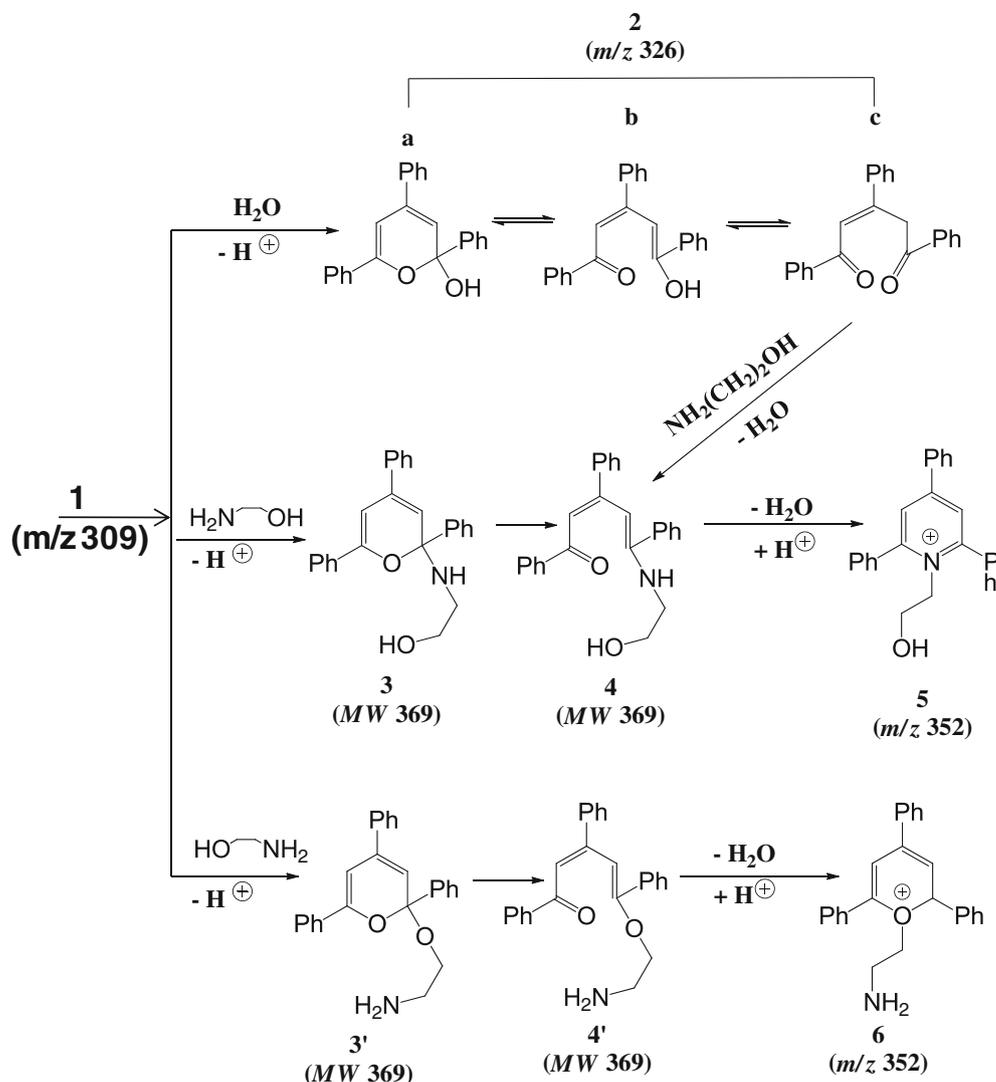
tially: (1) The  $m/z$  370 ion is absent in the surface reaction (Figure 3a), (2) MS<sup>2</sup> product ion spectra of the ions of  $m/z$  352 show them to be structurally different i.e., the  $m/z$  352 product ion formed from the surface reaction fragments to give ions of  $m/z$  308 via the loss of ethylene oxide ( $MW$  44) whereas the solution phase-reaction product fragments to give ions at  $m/z$  308 (also by losing ethylene oxide) and  $m/z$  274, which is due to the loss of benzene ( $MW$  78), and (3) ions at  $m/z$  327 and 349 are absent in the solution-phase reaction (Figure 3b).

In solution, the pyrylium and amine reaction is reported to proceed via a 2H-pyran intermediate (3, Scheme 2), which has been identified in this study as the  $m/z$  307 ion (MS/MS analysis indicate it is ethanolamine adduct of the parent pyrylium cation, Figure 4a). Product pyridinium cation is formed by gradual loss of water from the ring-opened 2H-pyran intermediate 4. The absence of the 2H-pyran interme-

diated from the surface reaction mixture was unexpected since it is very stable. Its absence suggests that solvent effects influence its stability (discussed later) or that a new pathway is available for the surface reaction. Inspection of MS (Figure 3a) obtained from the surface reaction revealed three other peaks ( $m/z$  327, 349, and 388) which are also absent from the solution-phase reaction product (Figure 3b). These ions corresponded respectively to the protonated, sodiated and ethanolamine adduct of the pseudobase intermediate (2), which has also been found to be involved in certain reactions of pyrylium with amine [37] (MS/MS data for each species is provided and interpreted in Figure S4, Supporting Information). This intermediate is formed by the interactions of the pyrylium cations with traces of water present at the surface of the nominally dry ethanolamine. Abstraction of a proton by the amine present in high abundance affords the neutral pseudobase intermediate 2a (Scheme 2), resonance



**Figure 3.** Mass spectra comparing products of (a) surface reaction and (b) bulk solution-phase reaction between 2,4,6-triphenylpyrylium cation ( $MW$  309) and ethanolamine ( $MW$  61). In each case, positive mode nanospray ionization was used for mass analysis, and solutions were made in methanol/water (1:1). 2,4,6-Triphenylpyrylium cations were landed for 1 h in the surface reaction. MS/MS of the product ion at  $m/z$  352, using 35% (manufacturer's unit) collision energy are shown as inserts, as well as MS<sup>3</sup> product ion spectra via 308. Exact mass of 352.17035 was measured (with an error of 2.2 ppm) for the product ion (chemical formula  $C_{25}H_{22}NO$ ) using an exactive instrument. Peaks at  $m/z$  476 and 537 in Figure 3b are assigned to reaction products of an impurity 2-bromoethylamine present in the commercial ethanolamine



Scheme 2. Proposed surface reaction mechanism via the pseudobase intermediate (**2**) for pyrylium ion to pyridinium ion conversion is compared with the solution-phase reaction mechanism via 2H-pyran (**3**) following Katritzky [37]; an alternative mechanism (**3'** → **6**) leading to the new isomeric products observed in solution is also proposed

forms of which are shown as 2b and 2c. The final product of reaction at the surface ( $m/z$  352) is then formed in a slow reaction of the pseudobase **2c** with ethanolamine, evidence of which is seen in the pseudobase-ethanolamine adduct formed at  $m/z$  388. Note that the  $m/z$  388 ion observed for the solution-phase reaction (Figure 3b) is a different species; namely the hydrated adduct of  $m/z$  370 ion (compare Figure 4c and d).

Owing to differences in reaction conditions and mechanisms, tandem MS was conducted on the reactions products ( $m/z$  352) in order to investigate any structural differences that might exist between the surface-generated pyridinium cation and that formed in the bulk solution-phase reaction. As has already been explained, the solution-phase reaction product ( $m/z$  352) fragments upon collision-induced dissociation (CID) to give ions at  $m/z$  308 (via the loss of ethylene oxide) and 274 (via the loss of benzene) whereas the surface

product dissociates only to give the  $m/z$  308 ion. This striking difference strongly suggests that the precursor ions are structurally different. This is in turn rationalized by the fact that the solution-phase reaction intermediate at  $m/z$  370 is comprised of two isomers (**3** and **3'**). The hydroxylamine base can act as either a N-centered or an O-centered nucleophile and it does this competitively, the O-centered reaction intermediate competing less effectively than the N-centered nucleophile. The isomeric product (**6**) resulting from dehydration of the O-centered reaction intermediate (**3'**) cannot lose ethylene oxide when subjected to CID. The gas-phase ion at  $m/z$  352 formed upon CID of  $m/z$  370 ion fragments predominantly to give ion at  $m/z$  274 through the loss of a benzene molecule when collisionally activated in an  $MS^3$  experiments (Figure 4b). This gives definitive confirmation that the dehydrated product from **3'** is responsible for the fragment ion at  $m/z$  274 observed in the  $MS^2$  product ion

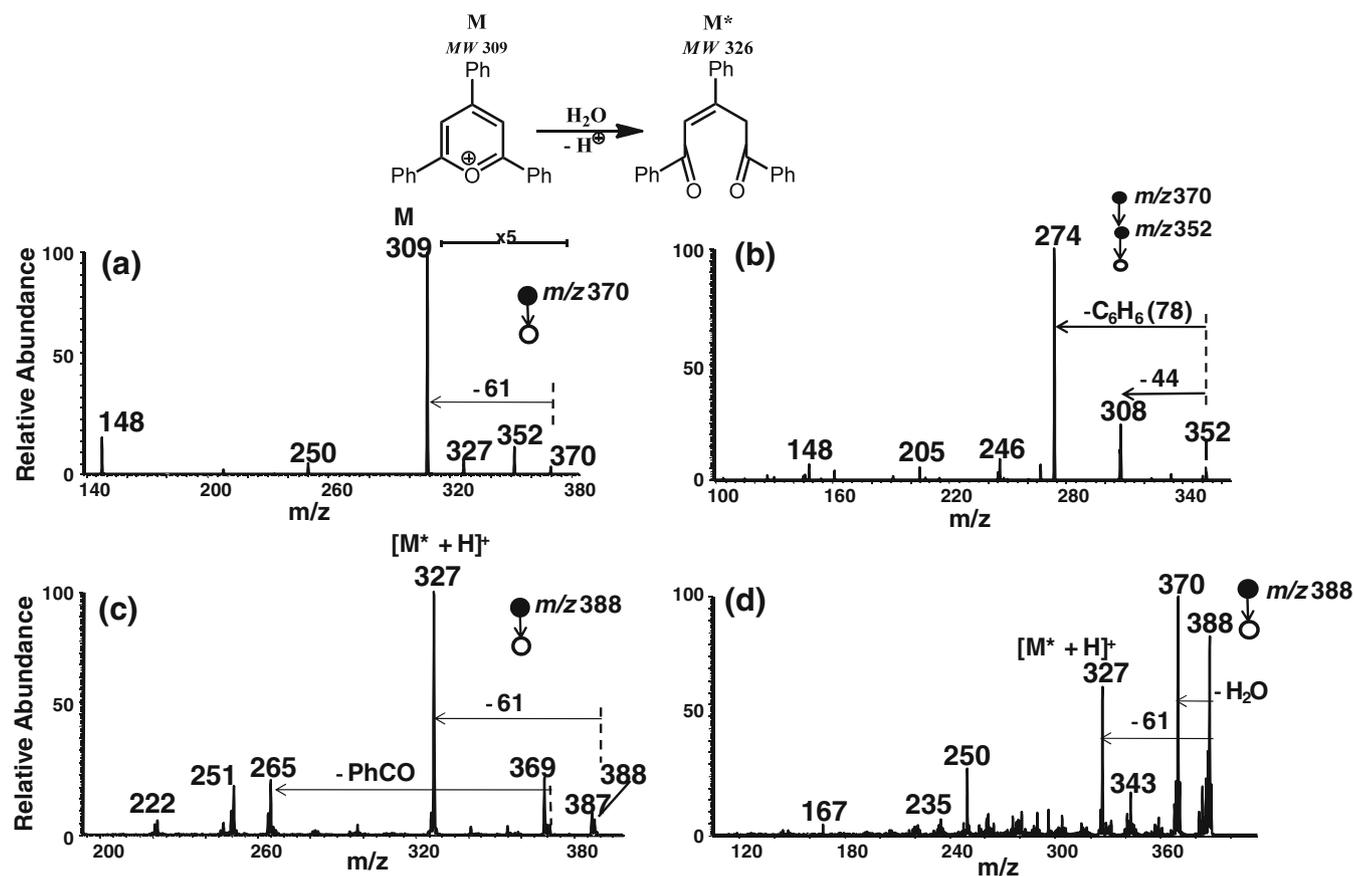


Figure 4. (a) MS<sup>2</sup> and (b) MS<sup>3</sup> product ion spectra of the *m/z* 370 via *m/z* 352 ions for solution-phase reaction condition; MS/MS product ion spectra of the *m/z* 388 ions formed (c) at surface and (d) in bulk solution phase

spectrum at *m/z* 352 for the solution-phase reaction. The tandem mass spectrometry (insert, Figure 2a) of the product ion (*m/z* 352) formed during the surface reaction, clearly suggests that only one major isomer of the solution-phase products is generated. It is assumed that only Compound 6 will give rise to the *m/z* 274 ion and so the absence of this fragment ion indicates the absence of Compound 6 during the surface reaction.

The presence of mixed structural isomers in the solution-phase reaction was further investigated by reaction of the pyrylium cation with *n*-butylamine, which contains only the N-centered nucleophile. The results of this solution-phase reaction were also compared with those for reaction at surface. Again, the 2H-pyran (*m/z* 382) reaction intermediate was observed only for the solution-phase reaction and the pseudobase intermediate (*m/z* 349) for the surface reaction (Figure S5, Supporting Information). MS/MS spectra of the pyridinium product ions at *m/z* 364 (both at surface and in solution) were identical, giving a major fragment at *m/z* 308 via 1-butene neutral loss. These findings suggest that no mixed isomers are formed in solution for *n*-butylamine, and support the interpretation that the presence of an O-centered nucleophile in ethanolamine caused the different fragmentation patterns observed for the solution-phase product at *m/z* 352. The pyrylium reaction with *n*-butylamine at the surface,

however, yielded a second (minor) product at *m/z* 365 (Figure S6, Supporting Information). This is believed to have formed via ammonia loss (instead of water after pseudobase and amine reaction) leading to a transmethylation reaction. Such transmethylation reactions appear to be prominent at the surface for long chain amines ( $\geq C4$ ) since similar effects have been observed for D-lysine reaction with pyrylium under the same experimental conditions [29].

The involvement of pseudobase intermediates in pyrylium reactions with amines is not uncommon, and has been reported for bulk phase reactions of 2,4,6-triphenylpyrylium with lysine [37]. In some cases of pyrylium reaction with amines, the type of intermediate involved (either pseudobase or 2H-pyran) is dependent on whether or not excess amine is used [44]. In the present study, mass spectra recorded after directing solvated rather than dry pyrylium cations onto condensed phase ethanolamine showed that both the pseudobase and the 2H-pyran intermediates were formed at the surface (Figure S7, Supporting Information). (This condition was achieved by not supplying heat to the drying tube, and so positively charged droplets instead of dry ions were landed.) This observation rules out the possibility that a pseudobase intermediate might be formed on the surface because of the lack of amine. It also indicates that the 2H-pyran intermediate might be stable in the

presence of solvent molecules, and hence its absence from the solvent-free surface reaction conditions.

H/D exchange experiments were also conducted to investigate the structural differences suggested by the MS data. To do this,  $d_4$ -methanol/water (5:1, vol/vol) was used to rinse the ion spot from the surface. This same solution was also used as a solvent for the bulk solution-phase reaction. Up to three protons were exchanged in the both surface and solution-phase products (Figure S8, Supporting Information) owing to H/D exchange in the course of isomerization of the reaction intermediates present in each case of the reaction conditions. The results also indicate that the solution-phase reaction product underwent more H/D exchange compared with the product formed on the surface.

## Conclusion

We have presented a methodology by which solvent-free ion chemistry and reaction mechanisms can be studied at atmospheric pressure. Insights into the mechanism of the reaction involving 2,4,6-triphenylpyrylium cations and ethanolamine have been acquired. The studies show that the atmospheric pressure surface reaction produced just one of the two isomers of the bulk phase reaction products. This is supported by the following experimental findings: (1) SERS results indicate that surface product occurred during the surface reaction not during washing prior to MS analysis, (2) the MS fragmentation pattern of the solvent-free product was found to be different from that of the solution-phase reaction product, and (3) H/D exchange results provide supporting evidence for the reaction intermediates deduced from the MS data, showing the intermediates can exchange up to three hydrogen atoms; the same results also indicate that the solution-phase reaction product readily undergoes H/D exchange compared with the product formed at the surface. The differences found in the MS and H/D exchange experiments may be accounted for by the presence of an additional minor isomer found in the solution-phase reaction. An explanation as to why the solution-phase reaction produces two distinct products has also been given: two isomers of the solution-phase reaction intermediate are proposed: N-centered and an O-centered ethanolamine-substituted 2H-pyran intermediates. The surface reaction on the other hand is proposed to proceed through the unreactive pseudobase intermediate, which presumably reacts exclusively via the more reactive N-centered nucleophile of ethanolamine. Analogously to the increase in gas-phase ion/molecule reaction rates observed upon solvent removal, here a similar increase in reaction rates can be expected under the dry surface reaction conditions although rate enhancement is not the subject of this work.

The study adds support to the observation that chemical reactions within organic layers and at interfaces between organic films and an aqueous phase or the atmosphere often exhibit markedly different reactivity to that shown by the same compounds in bulk solution phase. Unexpectedly, gas-phase

2,4,6-triphenylpyrylium ions directed onto a dried film of ethanolamine yielded distinctive and regiospecific route to 2,4,6-triphenylpyridium cation upon reaction with ethanolamine. On the other hand, some unwanted reaction products have been found to be associated with the solution-phase reaction. The procedure reported here thus allows an effective way to create and study the reactivity of organic ions at thin films and illustrates how this non-traditional way of processing materials can also provide new information on novel chemistry. Specifically, surface modification using the ambient soft landing is particularly interesting because it allows ion chemistry to be investigated at atmospheric pressure; it also provides a means to purify ions, direct them electrically, as well as to focus and deposit the ions onto a surface at a specified location. Because the ions are processed outside the mass spectrometer at atmospheric pressure, the analysis of the treated surface using surface techniques such as Raman spectroscopy is straightforward and requires no additional instrumental modifications, in much the same way as when fluorescence and atomic force microscopy are employed.

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