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Molecular Weight Growth in the Gas Phase
Reactions of Dehydroanilinium Radical
Cations with Propene

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Abstract

Protonated aniline – one of the simplest nitrogen-bearing molecules – is speculated to be present within Titan’s atmosphere, where it could play a role in molecular weight growth chemistry. To investigate this possibility, this paper examines the reactions of propene with distonic radical cations derived from protonated aniline. The reaction kinetics, products and branching ratios of these distonic radical cations (i.e., 2-, 3-, and 4-dehydroanilinium radical cations) are measured in the gas phase and ion-trap mass
spectrometry and calculations (M06-2X/6-31G(2df,p) and G3X-K) are used to characterize each reaction. The reaction efficiencies for the 2-, 3-, and 4-dehydroanilinium radical cations are reported as 30.7 (±3.1)%, 2.4 (±0.5)%, and 2.1 (±0.4)%, respectively (with 50% absolute accuracy). The 4- and 3-dehydroanilinium radical cations undergo addition of propene followed by (i) methyl radical loss forming ammonio styrene cations ($m/z$ 120) and (ii) ethylene loss pathways forming the ammonio benzyl radical cation ($m/z$ 107). The 4-dehydroanilinium reaction favours the methyl loss over ethylene loss whereas the reverse is true for 3-dehydroanilinium. In contrast, the 2-dehydroanilinium radical cation reacts with propene to purportedly form amino tropylium cation ($m/z$ 106) by ethyl radical loss and methyl amino tropylium cation ($m/z$ 120) by methyl radical ejection. The energies of all minima and transition states leading to predicted dissociation products are below the energy of the initial reactants providing plausible pathways at lower temperatures of Titan’s atmosphere.

**Introduction**

Molecular weight growth processes are a key aspect of the chemistry of extraterrestrial environments\(^1\)–\(^5\). In particular, the atmosphere of Titan is rich in tholins, which are complex molecular aggregates which, collectively, give rise to the opaque atmosphere.\(^1\) Measurements by the Cassini space probe revealed that ions, and radical ions, are abundant in Titan’s upper atmosphere\(^1,2\) and are believed to be significant contributors to its molecular weight growth chemistry\(^3\) – these ions are known to contain nitrogen.\(^6\) We therefore require a further understanding of the chemistry of nitrogen-containing aromatic ions in order to describe the atmospheric composition of Titan.

Neutral radical species are important in many molecular weight growth reactions, particularly those occurring in higher-temperature environments such as in combustion reactions\(^7\)–\(^9\) and in circumstellar envelopes.\(^8,9\) Some direct evidence for viable low-temperature neutral-radical molecular weight growth processes have been recently uncovered,\(^10,11\) however, there
remains major scope for revealing the key molecular weight growth pathways relevant in the atmosphere of Titan. Our particular focus in this paper is the chemistry of distonic radical ions, where the radical site and charge site are spatially separated on the molecule. These radical ions can combine the low-temperature reactivity of ions with the propensity towards molecular weight growth chemistry of neutral radicals.\textsuperscript{12-15} In some cases, distonic radical ions can be more stable than their conventional radical-ion counterparts (where the charge and spin are collocated)\textsuperscript{15,16} and furthermore, aromatic distonic radical ions can have high barriers towards isomerization,\textsuperscript{12,15} indicating that they could exist as stable intermediates in the atmosphere of Titan. The Cassini ion neutral mass spectrometer (INMS) detected signal at $m/z$ 94, which modeling studies\textsuperscript{2} have assigned to a molecular formula consistent with protonated aniline ($\text{C}_6\text{H}_7\text{NH}^+$), and $m/z$ 93 is assigned in this paper\textsuperscript{2} to both $\text{C}_7\text{H}_9^+$ and $\text{C}_6\text{H}_7\text{N}^+$, the latter of which is the molecular formula for aniline radical cations. It is noted that anilinium and pyridinium are speculated to be present in the upper atmosphere of Titan based only on their $m/z$ values.\textsuperscript{1,2} The relative energies of the isomers of the dehydroanilinium radical cation, including the three distonic radical cation targets of this paper, and transition states between them, are shown in Figure 1.

High-energy reactions with small radicals, interactions with high-energy photons and interactions with cosmic rays are plausible sources for the formation of these higher-energy isomers. In particular, Lyman-\(\alpha\) (121.6 nm) photons\textsuperscript{17,18} may lead to C-H bond dissociation of aromatic ions, such as the anilinium or pyridinium ion, to form distonic radical ions. Though this dissociation pathway has yet to be verified experimentally at 121.6 nm, VUV photolysis of benzene at 193 and 157 nm leads to loss of atomic hydrogen,\textsuperscript{19} suggesting that analogous processes are possible for similar aromatic ions. Figure 1 shows that the conventional radical cation of aniline is the most stable, however small yields of the reactive distonic isomers may be important in the molecular weight growth chemistry in Titan’s atmosphere.

This paper details the reactions of the 2-, 3-, and 4-dehydroanilinium radical cations with
Figure 1: Relative energies of the isomers of the dehydroanilinium radical cation and transition states between them, in kcal/mol, calculated in this study using M06-2X/6-31G(2df,p). The conventional radical cation, at 0.0 kcal/mol, is the lower in energy.

propene. The co-reactant propene has also been identified in Titan’s stratosphere.\textsuperscript{20,21} For these reactions, branching ratios and reaction kinetics are experimentally measured at approximately 300 K and 2.5 mTorr. Theoretical analysis using quantum chemical calculations is performed assuming a temperature of 0 K and a collision-free environment.

Experimental

Ion trap mass spectrometry

The reactions of the 2-, 3-, and 4-dehydroanilinium radical cations with propene were investigated using a modified linear quadrupole ion-trap mass spectrometer (Thermo Scientific LTQ XL). This instrument was equipped with an alternate gas supply which allowed neutral co-reactants, in this case propene (99.99\%, Sigma Aldrich), to be introduced into the ion trap seeded in the helium buffer gas. The flow bypassed the standard internal splitter input and instead was controlled using a mass flow controller (MKS GE50A, 5 sccm) set to a flow rate of 1.3 sccm to maintain the optimal pressure within the ion trap (\textasciitilde 2.5 mTorr). Flows were maintained for a minimum of 12 hours prior to experiments to ensure stable gas conditions in the ion trap. The instrument also had a quartz window positioned at the rear of the
vacuum chamber, allowing laser access through the back of the trap, along the principal axis, and allowing irradiation of stored ions. The laser was a frequency-quadrupled Nd:YAG laser (266 nm, Continuum Minilite). A more detailed description of the instrument can be found in reference 22. The Q-switch of the laser was internally triggered approximately 140 µs after the flashlamp was triggered by an external signal generated from the mass spectrometer. The laser is pulsed once per mass spectrometry cycle.

The iodoanilinium precursor ions were introduced \textit{via} electrospray ionization (ESI) of 2-, 3-, and 4-iodoaniline (98%, Sigma-Aldrich), as \( \sim 10 \, \mu \text{M} \) in methanol with \( \sim 1\% \) formic acid. These solutions were supplied at a flow rate of 5 µL/min, and the ESI source was operated in positive ion mode. Mass isolation of the \( m/z \) 220 precursor ions, and of the \( m/z \) 93 dehydroanilinium radical cations, was performed within a 1 Th window with a 0.250 \( q \) parameter. Typical instrument parameters were 4 kV electrospray voltage and 250°C capillary temperature, with the sheath gas flow set to 8 and the auxiliary and sweep gas flows both set to 0 (all in arbitrary units). Individual product mass spectra presented are averages of 1000 scans. The dehydroanilinium radical cations were generated \textit{in situ} from iodinated 2-, 3-, and 4-iodoanilinium precursor ions, by 266 nm laser photodissociation (PD). Once the dehydroanilinium radical cations had been isolated and stored, they were allowed to react with propene over timescales ranging from (nominally) 0.03 ms to 5000 ms. The mass isolation sweep occurred over a timescale of approximately 10 ms. Propene gas was introduced from separate sample tanks corresponding to mole fractions varying from \( \sim 10^{-4} \) to \( \sim 10^{-2} \) in helium, corresponding to ion trap number densities in the range \( \sim 10^{11} - 10^{12} \, \text{cm}^{-3} \). These values are based on an ion trap pressure of 2.5 mTorr, as reported by Harman \textit{et al.} \( ^{23} \) This value is assumed to have a systematic uncertainty of \( \pm 50\% \).\(^{15} \) As the concentration of propene vastly exceeded that of the dehydroanilinium radical cations, the reaction kinetics could be well approximated as \textit{pseudo}-first order, depending only on the change in radical cation population with respect to time. Measurements of the reaction kinetics for each radical were repeated 4 times for each propene concentration with each single kinetic data
point representing the average of about 25–30 mass spectra.

From these data, plots were constructed by integrating the product peaks of interest over a 1 Th window, and then normalized by dividing by the total integral over $m/z$ 50 and 300, as the total ion count. These normalized product peaks were then averaged over scans, and plotted over time to show the reaction kinetics. The time dependence of the concentration of target distonic radical ions at $m/z$ 93, and primary products, were fit to single exponential functions with constant offset using the Levenberg-Marquardt algorithm$^{24,25}$ as implemented in pro Fit (QuantumSoft). Data were weighted by their 95% confidence interval values. Then, these pseudo-first-order rate coefficients (reciprocal time constants) were plotted against propene concentration and fitted by linear regression. The slope of these linear functions provided the second-order coefficient for each reaction, which could then be cast as reaction efficiencies by dividing by the estimated collision rate using either a Langevin$^{26,27}$ or a parametrized trajectory model proposed by Chesnavich and Su.$^{28}$

**Quantum chemical calculations and modeling**

Quantum chemical calculations were employed in order to aid in product assignment, elucidate product formation pathways and rationalize branching ratios. Gaussian 09$^{29}$ was used to calculate structures and energies for minima, transition states, intrinsic reaction coordinate (IRC) scans and relaxed redundant coordinate scans. These calculations were initially performed using density functional theory (DFT) with the M06-2X functional$^{30,31}$ and 6-31G(2df,p) basis set. Points of particular interest were recalculated with the composite G3X-K method.$^{32}$ Transition states were verified by first confirming the existence of just one imaginary frequency and then by visualization of the imaginary frequency. In cases where the visualization was unclear in determining which minima were linked by a given transition state, IRC calculations were performed to validate that the relevant minima were linked to the transition state. The reported 0 K energies include a zero-point vibrational energy correction. Structures in potential energy schemes are labelled A for initial adducts, I for
other intermediates, and $P$ for products. Superscript prefixes ‘o’, ‘m’ and ‘p’ denote whether the molecule is formed in the reaction of the ortho-, meta-, or para-dehydroanilinium radical cation. Subscript suffixes ‘E’, ‘Z’, ‘o’, ‘m’, and ‘p’ refer to local stereochemistry of an intermediate, appearing only in cases of broken degeneracy of reaction pathways relative to the 4-dehydroanilinium reaction with propene.

The computational kinetics for key pathways in the 4-dehydroanilinium + propene energy surface was examined in more detail to rationalize the branching ratios, using an RRKM analysis. This analysis involves calculating reaction rates taking into account the effect of the density of active rovibrational states, using the equation:

$$k(E) = \sigma c \int_{E_0}^{E} \frac{\rho_r(\epsilon) d\epsilon}{\rho_r(E)}$$

where $k(E)$ is the microcanonical rate constant at energy $E$, $\sigma$ is the reaction path degeneracy, $\int_{E_0}^{E} \rho_r(\epsilon) d\epsilon$ is the sum of states for the transition state from the barrier height $E_0$ to $E$, and $\rho_r$ is the density of states of the reactant. $c$, the speed of light, is the appropriate constant to use here as the energies and state densities are cast in units of cm$^{-1}$, and cm, respectively. The integral in the numerator corresponds to the sum of available states for the transition state. The integrated densities of states of the transition states also took into account a tunneling correction, modeled through an unsymmetrical Eckart barrier. Calculations of state densities was undertaken using the MultiWell 2017 suite of programs. Vibrational modes were approximated as either harmonic oscillators or as hindered rotors, by visual inspection in GaussView 5.0.8. Hindered rotor potentials were calculated from relaxed coordinate scan of the relevant rotor with a step size of 20 degrees. A Fourier analysis of up to at most 6 sine and cosine terms was then used as input into the MultiWell subprogram Densum, along with the remaining modes treated as harmonic oscillators.
Results and discussion

Synthesis of dehydroanilinium radical cations

The iodoanilinium cations ($m/z$ 220, [M+H]), ionized by electrospray ionization (ESI), were isolated and stored in the ion trap and subjected to photodissociation (PD) with a 266 nm laser pulse. Product ions formed at $m/z$ 93 correspond to a neutral loss of 127 Da, indicating C–I bond homolysis. As reported previously in the case of the photolysis of iodopyridinium cations, the production of distonic radicals is efficient at ~5%.

Product mass spectra

Figure 2 shows the product mass spectra of $m/z$ 93 synthesized from o-, m-, and p-iodoanilinium after being allowed to react with propene for 500 ms storage time. All three radical cations undergo addition reactions with neutral propene to form adduct ions at $m/z$ 135. The product mass spectra contain a product ion from the methyl loss channel from this adduct, at $m/z$ 120. Also present is a minor hydrogen atom abstraction product at $m/z$ 94, assigned as protonated aniline. In the case of both 3- and 4-dehydroanilinium, a strong signal at $m/z$ 107 indicates the loss of ethylene (28 Da) from the initial adduct at $m/z$ 135 and this channel is absent in the 2-dehydroanilinium case. A product signal at $m/z$ 106, which indicates the loss of an ethyl radical ($C_2H_5^•$, 29 Da) is unique to the 2-dehydroanilinium case. Peaks marked with an asterisk denote side reactions with oxygen including $m/z$ 125, 134 and 167 as verified in the supporting information. The $m/z$ 125 and 167 peaks are speculatively assigned to products of $O_2$ addition (+32 Da) to the dehydroanilinium radical cation in the case of $m/z$ 125 and to the propene addition product in the case of $m/z$ 167 ($m/z$ 135 + 32 Da). The $m/z$ 134 peak is possibly the result of $O_2$ addition followed by HO$_2$ loss from the adduct at $m/z$ 135. These processes are in accord with those previously observed in the reactions of distonic radical ions with oxygen.
Figure 2: Product mass spectra of (a) 4-, (b) 3-, and (c) 2-dehydroanilinium radical cations ($m/z$ 93) with propene after 500 ms storage time. Adduct formation ($m/z$ 135), as well as methyl loss ($m/z$ 120) and ethylene loss ($m/z$ 107) from the adduct dominate the former two reactions, whereas ethyl radical loss from the adduct ($m/z$ 106) dominates the latter, along with small amounts of undissociated adduct and methyl loss. Asterisks denote competing chemistry with O$_2$. Minor peaks present at $m/z$ 160 and $m/z$ 145 in (a) and (b) are assigned to secondary propene addition to a minor ammonia loss ($m/z$ 118) channel.

**Reaction kinetics and branching ratios**

To explore the reactivity of these dehydroanilinium distonic ions with propene, the kinetics of each system were investigated. By changing the ion storage time, the rates of disappearance
of the initial radical ions were monitored along with the appearance of product ions. Figure 3 displays the reactant radical ion decays, as well as the growth of the three most abundant product ions. In Figure 3(c) the $m/z$ 93 signal decays to a significant baseline offset value of 0.46 and this is attributed to the presence of the conventional radical cation of aniline, formed by isomerization in the prompt timescales following photolysis, which is unreactive to propene on this timescale. The reactive 2-dehydroanilinium distonic radical cation does react and contributes to the decaying signal. Photoinduced isomerization is significantly reduced in the 3- and 4-dehydroanilinium systems. Figure 1 shows the barrier to isomerization between the 2-dehydroanilinium radical ion and the conventional aniline radical ion is 42 kcal/mol. As a guide, the phenyl iodide C–I bond energy is 67 kcal/mol and with the absorption of a 266 nm photon corresponding to 107.5 kcal/mol, the residual energy following bond homolysis is $\sim$40.5 kcal/mol, which is approximately the same as the barrier height and thus a reasonable explanation for this heightened degree of photoinduced isomerization. Due to the large connecting barriers, it is unlikely that the different distonic radical cations are isomerizing between each other.

The decaying population of the reactant ($m/z$ 93) follows a trajectory that is well-fitted by a single exponential function with constant baseline offset (accurate to better than 0.5%) and the decay time constants (reciprocal rate constants) match the time constants for the growth of the products. These data are shown for each case in Table 1. There is a degree of non-randomness in the difference between the fitted function and the data points (this difference is referred to here as the residual) and this is particularly noticeable for 4-dehydroanilinium, which show some systematic oscillation over the reaction timescale. A similar small bi-exponential trend in the residual values was also pointed out in the reactions of dehydropyridinium radicals with propene. However with varying propene concentration, as is shown in Figure 4, all three systems follow a linear trend for the reaction rate, confirming that the vast majority of the reactivity is adequately described by pseudo-first order behaviour, with respect to propene. The slope of each line from these fits in Figure 4 is the
experimental second-order rate coefficient for each reaction. The small non-zero intercept values are attributed to the presence of reactive impurities, including background oxygen. Table 2 lists the ultimate product branching values from the exponential growth fitted to the product ions. Unique among these three systems, the 2-dehydroanilinium product mass spectrum does not show a stabilized adduct product ion. For the 2-dehydroanilinium system, the abundant and unique ethyl radical loss pathway forming \( m/z \) 106 arises from prompt dissociation of the adduct compared with the other two reactions as will be detailed further below.

Table 1: Fitted single exponential time constants (to 95% confidence) for the 1st-order kinetic plots shown in Figure 3, for the reactant radicals and their major products.

| Radical          | (m/z) | Time Constant / ms |
|------------------|-------|--------------------|
| 4-dehydroanilinium | 93    | 34.8 ± 0.2         |
|                  | 107   | 34.0 ± 0.8         |
|                  | 120   | 34.3 ± 0.7         |
|                  | 135   | 34.0 ± 0.5         |
| 3-dehydroanilinium | 93    | 26.0 ± 0.3         |
|                  | 107   | 25.8 ± 0.7         |
|                  | 120   | 25.9 ± 0.9         |
|                  | 135   | 25.5 ± 0.3         |
| 2-dehydroanilinium | 93    | 25.6 ± 0.5         |
|                  | 106   | 25.2 ± 0.6         |
|                  | 107   | 25.8 ± 1.4         |
|                  | 120   | 25.7 ± 1.0         |

Comparison of the three systems in Figure 4 reveals that the rate coefficients increases with decreasing radical-charge separation, with the 4-dehydroanilinium reaction as the slowest and the 2-dehydroanilinium reaction as the fastest. The reaction efficiencies can be calculated from these second order rate coefficients using different collisional models and are presented in Table 3. In the Langevin model, the reactants are considered to be pointlike: one species is charged and the other species is neutral, polarisable, but with no permanent dipole moment.\(^{26,27}\) The 0.366 D dipole moment of the propene molecule\(^ {43}\) can be accounted
Figure 3: Kinetic plots of the (a) 4-, (b) 3-, and (c) 2-dehydroanilinium reactions with propene, following the four major ions. For (a) and (b), the propene concentration is $1.02 \times 10^{12} \text{ cm}^{-3}$, and (c) $1.05 \times 10^{11} \text{ cm}^{-3}$. Uncertainty in individual data points are significantly less than the size of the data points (at 95% confidence). The top trace in each plot shows the residuals for the single exponential fit with constant baseline offset.

for using the parametrized trajectory model of Chesnavich and Su. As including the dipole effects increases the calculated collision rate, the Langevin reaction efficiencies are marginally greater. In either case, while the reaction efficiencies of the 4- and 3-dehydroanilinium + propene systems are relatively low and of similar size, the 2-dehydroanilinium reaction with
Figure 4: Dependence of the *pseudo*-first-order rates of each reaction with respect to propene concentration.

Propene is an order of magnitude faster. A possible rationalization for this marked difference in reaction efficiency can be found by comparing the (vertical) electron affinities of each radical cation, as shown in Table 3. While the electron affinities of the 4-dehydroanilinium (7.37 eV) and 3-dehydroanilinium (7.55 eV) radical cations are of similar magnitude, the 2-dehydroanilinium radical cation has an electron affinity of 8.61 eV, more than 1 eV higher than either of the other radical cations. This increased electrophilicity may explain the significantly increased reactivity of the 2-dehydroanilinium radical cation towards the nucleophilic π-bond in the propene molecule. Indeed, the 31% reaction efficiency of the 2-dehydroanilinium + propene system, even at room temperature, hints that it may be an efficient reaction in the low-temperature molecular weight growth of aromatic ions. Further rationale for the enhanced reactivity of the 2-dehydroanilinium species may arise from the unique reaction pathways afforded to it by the close proximity of the amino group to the radical site, as will be explored in the next section.
Table 2: Experimental branching ratios between the major product channels resulting from adduct formation in the 4-, 3-, and 2-dehydroanilinium reaction with propene. Note that these ratios represent branching between only these channels, and do not account for other minor channels that may result from reactions with impurities. Uncertainties are 95% confidence intervals.

| Loss Channel | 4-Dehydroanilinium | 3-Dehydroanilinium | 2-Dehydroanilinium |
|--------------|---------------------|---------------------|---------------------|
| None (adduct)| 49% ± 1%            | 37% ± 2%            | 19% ± 1%            |
| H atom       | 4% ± 2%             | 4% ± 1%             | N/A                 |
| Methyl       | 32% ± 1%            | 25% ± 1%            | 11% ± 1%            |
| Ethylene     | 16% ± 1%            | 35% ± 3%            | N/A                 |
| Ethyl        | N/A                 | N/A                 | 71% ± 1%            |

Table 3: Second order rate coefficients, and reaction efficiencies for the three reactions calculated using both a Langevin and parametrized trajectory collision model. Uncertainties are reported to 95% confidence. Note that all values are reported with an estimated systematic ±50% relative error arising from uncertainty in the ion trap pressure.

| Molecule + Propene | Rate Coefficient / $10^{-11}$ cm$^3$ s$^{-1}$ | Langevin Efficiency | Trajectory Efficiency |
|---------------------|-----------------------------------------------|---------------------|-----------------------|
| 4-Dehydroanilinium  | 2.4 ± 0.4                                     | 2.2% ± 0.4%         | 2.1% ± 0.4%           |
| 3-Dehydroanilinium  | 2.8 ± 0.5                                     | 2.6% ± 0.5%         | 2.4% ± 0.5%           |
| 2-Dehydroanilinium  | 35.8 ± 3.6                                    | 32.9% ± 3.3%        | 30.7% ± 3.1%          |

Quantum chemistry calculations

To elucidate the key mechanistic steps for these reactions, quantum chemistry calculations were performed to determine the potential energy landscapes using DFT with the M06-2X functional and 6-31G(2df,p) basis set. Figure 5 presents a potential energy network of the 4-dehydroanilinium reaction with propene, where each structure is a local minimum in the potential energy surface and each transition state is represented by a line between two minima. The addition of the radical to the double bond of propene occurs via a submerged barrier; this means that the energy of this early transition state is lower than the energy of the separated reactants (or products), indicating the formation of a van der Waals complex. Subsequently, this addition forms either a linear or branched adduct, from which there are many possible pathways.
Figure 5: Graph of the minima and transition states considered in the 4-dehydroanilinium reaction with propene, with major transition states shown with red lines. All energies in kcal/mol, calculated using M06-2X/6-31G(2df,p). Energies are reported relative to the initial reactants. “vdW” denotes the existence of a van der Waals complex along the reaction coordinate.
The key pathways from Figure 5 were also calculated at the G3X-K level of theory. Figure 6 shows these recalculated values in a vertical potential energy scheme. The initial adducts \( pA1 \) and \( pA2 \) will undergo a rapid isomerization \( \text{via} \) the spiro structure \( pI1 \) such that any information about the initial attachment site of the radical will likely to be lost. Both initial adducts can undergo a hydrogen shift to form either a linear \( (pI2) \) or a branched \( (pI6) \) resonance-stabilized radical. Both \( pA2 \) and \( pI2 \) can lose a methyl radical, leaving an 4-ammonio styrene cation \( (pP1) \) as the product ion. Alternatively, from the linear adduct, the system can undergo a ring-mediated hydrogen shift \( \text{via} \) \( pI3 \) to form the \( \gamma \)-radical \( pI4 \). From here, the loss of ethene leaves a resonance-stabilized 4-ammonio benzyl radical cation \( (pP2) \).

A hydrogen atom loss pathway following cyclization to form an 5-ammonio indane cation \( (pP3) \) from \( pI4 \) appears energetically plausible, however there is scant signal at the corresponding \( m/z \) 134 product ion in the experimental results (and this little product signal is attributed to a background oxygen side reaction, as mentioned above). The pathway to form an 5-ammonio indane cation is marginally lower in energy than the related pathway to form an 4-ammonio benzyl radical cation \( \text{via} \) the loss of ethene, with the latter observed as a major product. To understand this further, it is required that entropic factors be taken into account and, as might be expected, the formation of the second ring comes at significant entropic cost to the system.

The effect of entropy on these reactions can be quantified using RRKM theory. For key intermediates and transition states, the rigid rotor/harmonic oscillator (RRHO) approximation, along with hindered rotors to represent internal rotation, was used to calculate the densities of states and integrated densities of states for the minima and transition states, respectively. Figure 7 displays these data, as base-10 logarithms, for the hydrogen loss and ethene loss channels forming from \( pI4 \). By taking the ratio of base-10 exponents of the values displayed for a given transition state and the relevant minimum, and multiplying by the speed of light and reaction path degeneracy as shown in Equation 1, the reaction rate
can be calculated. As such, the integrated state-density for the final hydrogen-loss transition state is about three orders of magnitude less than for the limiting transition state for the ethylene-loss pathway, despite the similar energies of these transition states. Thus the H atom elimination is not a major product pathway for this reaction.

Figure 6: Potential energy schematic for the key pathways in the 4-dehydroanilinium reaction with propene. Energies, in kcal/mol, calculated using G3X-K theory.

Figure 7: Entropic scheme of the competing ethylene loss and hydrogen loss channels in the 4-dehydroanilinium reaction with propene. Transition states (red and green) show densities of states, and minima (purple) show integrated densities of states, both as base 10 logarithms. Degeneracy of the reaction path is not shown. All values calculated using G3X-K energies, and M06-2X/6-31G(2df,p) harmonic frequencies and rotor potentials.

By quantifying the rates of reaction over each transition state, it is possible to estimate the branching ratios of the products observed. In particular, the zero-pressure RRKM rate
of reaction from $^{p}I_{6}$ to $^{p}A_{2}$ was calculated as 9.0 s$^{-1}$, which is ample time for significant collision stabilization. This rate assumes that the temperature of the reactants is 0 K, as the effect of temperature is expected to be minor compared with the energy released upon reaction (as $kT$ at 300 K is less than 1 kcal/mol). Hence, if formed, $^{p}I_{6}$ is unlikely to undergo any further rearrangement. Assuming that $^{p}I_{6}$ does not undergo further reaction, RRKM theory was used to predict the product branching ratios of the 4-dehydroanilinium reaction with propene (assuming a collision-free environment). These data are presented in Table 4, alongside the experimentally determined branching ratios. The predicted fraction of $m/z$ 135 (at this point assumed to be just $^{p}I_{6}$) does not match the experimental number. This presumably indicates that buffer-gas collisional deactivation is significant for other adduct intermediates and not just the stability of the resonance-stabilized radical cation $^{p}I_{6}$. Based on the RRKM estimated $\sim10^4$ s$^{-1}$ decay rate of the initial adducts ($^{p}A_{1}$ and $^{p}A_{2}$) under collision-free conditions and the He buffer gas collision rate of $4.3 \times 10^5$ s$^{-1}$ (2.5 mTorr), tens to hundreds of collisions with helium atoms can remove energy from the adduct ion before it has a chance to decompose, stabilizing it. A full analysis of collisional stabilization is beyond the scope of this simple RRKM model. To compare the predicted branching ratio between the methyl and ethylene loss channels, a portion of the adduct population was assumed to be collision-stabilized to fit the experimental measured amounts of $m/z$ 135 (and $m/z$ 134). The $m/z$ 134 is not relevant to the RRKM calculation as it is deemed to be the result of a side reaction with background oxygen gas present in the trap (this assertion is experimentally supported, see Figure S1 in the Supporting Information). Furthermore, it was assumed that any partial collisional deactivation of the initial adduct would have no effect on the branching ratio. With these simple assumptions, an improved agreement between the theoretical and experimental branching ratios of the methyl loss (4-ammonio styrene cation) and ethylene loss (4-ammonio benzyl radical cation) is reached (Table 4), and this supports the idea that the calculations performed for this reaction capture the key product formation processes. Future efforts will involve a more extensive master equation
modeling on this surface, including the evaluation of k(T) values, to understand the effect and extent of collision stabilization. This should provide further insight into the crucial steps affecting back-dissociation and the overall reaction efficiencies.

Table 4: Experimental and computational branching ratios in the reaction of 4-dehydroanilinium radical cations with propene, showing results both with and without a consideration of deactivating collisions. Uncertainties are 95% confidence intervals.

| Loss Channel | Experimental Branching Ratio | Computational Branching Ratio (collisionless) | Computational Branching Ratio (deactivated proportion) |
|--------------|------------------------------|-----------------------------------------------|------------------------------------------------------|
| None (adduct)| 49.2% ± 1.4%                | 4.4%                                          | N/A                                                  |
| H atom       | 3.6% ± 1.9%                 | 0.2%                                          |                                                      |
| Methyl       | 31.7% ± 1.0%                | 62.2%                                         | 30.8%                                                |
| Ethylene     | 15.5% ± 1.0%                | 33.3%                                         | 16.5%                                                |

The 3-dehydroanilinium reaction with propene exhibits many similarities with the 4-dehydroanilinium + propene case, with the most significant difference being the reduction of symmetry when the charge and radical have a *meta* relationship. In most cases, the energies are subtly different and, as such, the equivalent key pathways were chosen as those described for the 4-dehydroanilinium reaction with propene. These pathways are shown in Figure 8. Though almost all of the energies of the key reactions are unchanged to within 0.5 kcal/mol, the transition states $^{m}A1 \rightarrow ^{m}I_{3_o}$ and $^{m}I_{3_o} \rightarrow ^{m}I4$ lie approximately 2 kcal/mol below their equivalents on the 4-dehydroanilinium surface. As G3X-K theory is known to have a precision of approximately 0.5 kcal/mol for barrier heights when benchmarked, the energy difference highlights an important chemical difference between the two systems. Due to the closer proximity of the radical site and protonated amino moiety, the radical site has increased electrophilic character. This is known to increase the rate of hydrogen abstraction in distonic radical cation/neutral reactions, and this effect could explain intramolecular hydrogen abstraction. Thus, the lowered transition states, which can be thought of as hydrogen abstractions by the radical site from the alkyl tail of $^{m}I_{3_o}$, can be rationalized.
by this effect. Though the 2 kcal/mol difference in the energy of the two aforementioned transition states represent a change of only approximately 10% of the energy of the state, relative to the entrance energy, it has a major effect on their integrated state densities, which change by nearly an order of magnitude. This rapid rate of change is due to the fact that the density of states of coupled harmonic oscillators scale to the power of one less than the number of vibrational modes. After taking this into account, even with the loss of reaction path degeneracy of the two transition states, the end result is still a significant net enhancement of this pathway. As this is the limiting junction to the ethene loss channel, this explains why the experimental data show a significant preference for the loss of ethene in the 3-dehydroanilinium reaction with propene, when compared with the 4-dehydroanilinium reaction.

Figure 8: Potential energy schematic for the key pathways in the 3-dehydroanilinium reaction with propene. Where there is loss of degeneracy from an equivalent pathway in the 4-substituted system, only the lowest energy possibility is shown. Energies, in kcal/mol, calculated using G3X-K theory.

The 2-dehydroanilinium radical cation exhibits markedly different reactivity towards propene than the 3- and 4-dehydroanilinium radical cations and this can be understood
from Figure 9. There is a strong energetic preference for the radical located on the adduct, after it forms through a submerged barrier, to abstract a hydrogen atom from the protonated amino moiety. This results from the fact that both the charge and radical site can conjugate through the ring, thus increasing the stability of the system. This increase in stability is such that almost all of the other transition states available to the system can be ignored. The system rapidly proceeds then to form the radical cation of either 2-n-propylaniline or 2-i-propylaniline. From this point, the system can undergo a multi-step ring-expansion to form three different substituted cycloheptatriene radicals. The loss of an ethyl or methyl radical then forms an aminotropylium cation (m/z 106), or a 3-methylaminotropylium cation (m/z 120), respectively. Ring expansion followed by methyl or ethyl radical loss are lower energy pathways overall than the corresponding alkyl radical losses to form benzylium cation species – hence, it is likely that the methyl and ethyl loss channels observed in the mass spectrum are indeed substituted tropylium cations.

To demonstrate that the 2-dehydroanilinium radical cation is the only distonic isomer that reacts via a pathway that involves the transfer of hydrogen atoms from the nitrogen atom following propene addition, mass spectra were recorded where each iodoaniline isomer was singly deuteronated rather than protonated. For deuterated 2-dehydroanilinium reacting with propene, the mass spectrum is shown in Figure 10. The corresponding deuterated 3- and 4-dehydroanilinium spectra are presented in the Supporting Information (Figure S2). As expected, the 2-dehydroanilinium reaction with propene is the only reaction that shows any evidence that deuterium is present on the neutral fragment lost. Interestingly, this transfer is only observed to a significant extent in the ethyl loss channel (m/z 107 and 108), where the peak ratio does not quantitatively match the 5:4 ratio that would be expected if the deuterium is randomly scrambled among the propyl tail and the amino group prior to ethyl radical loss. In the case of methyl loss (m/z 121), however, essentially no CH$_2$D is lost. It is unclear why this is the case. Possibly, this result could indicate that there is a significant kinetic isotope effect inhibiting deuterium transfer in these intermediates, or else
Figure 9: Graph of the significant minima and transition states considered in the 2-dehydroanilinium reaction with propene, with major transition states shown with red lines. For clarity, not all considered pathways are shown, with the lowest neglected pathway from a given minimum shown with a green arrow. All energies in kcal/mol, calculated using M06-2X/6-31G(2df,p). Energies are reported relative to the initial reactants. “vdW” denotes the existence of a van der Waals complex along the reaction coordinate.
that a non-RRKM process is taking place.

Future studies with propene-$d_6$ would provide further insight into the product branching between methyl loss and ethylene loss for both the 4-dehydroanilinium and 3-dehydroanilinium cases. Since D atom substitution typically hinders H-shift pathways, the formation of the $\gamma$-radical and hence the ethylene loss product channel is expected to be inhibited, whereas the direct CH$_3$ loss (CD$_3$ loss in the propene-$d_6$ case) pathway should be less affected. For 2-dehydroanilinium, reactions with propene-$d_6$ case may provide further insight into the formation of substituted tropylium cations, due to a required D-atom shift. This is opposed to benzylium cation pathways, which avoid this step. Thus, a reduction in methyl and ethyl loss channels for the 2-dehydroanilinium reaction would be indicative of the formation of substituted tropylium cations.

Ultimately, the fact that the reaction between propene and the 2-dehydroanilinium radical cation exhibits rich chemistry, with products absent in the other two cases, shows the importance of the ortho relationship between the protonated amino moiety and the radical site in providing a significantly more favourable pathway for the radical. Indeed, this reaction provides a possible mechanism for the formation of substituted tropylium cations at low temperatures, providing alternative pathways towards the synthesis of charged, nitrogenated polyaromatics leading to the formation of tholins in Titan’s atmosphere.

Figure 10: Mass spectrum of the reaction between singly deuterated 2-dehydroanilinium ($m/z$ 94) with propene, allowing a deuteron to be lost from the adduct ($m/z$ 135) in the case of ethyl radical loss, giving peaks at $m/z$ 107 and 108.
Conclusions

The reactions of the three dehydroanilinium radical cation isomers with propene were investigated with ion-trap mass spectrometry, quantum chemical calculations and statistical reaction rate theory. At room temperature and a pressure of 2.5 mTorr, all three reactions were spontaneous, and proceeded with reaction efficiencies exceeding 1%. Specifically, the 4-, 3-, and 2-dehydroanilinium reactions with propene had reaction efficiencies of, respectively, $2.1\% \pm 0.4\%$, $2.4\% \pm 0.5\%$, and $30.7\% \pm 3.1\%$ with collision rates calculated using the parametrized trajectory model of Chesnavich and Su (statistical uncertainties to 95% confidence). The order-of-magnitude difference between the reaction rate of the 2-dehydroanilinium radical cation and the two other distonic isomers was attributed to the significantly higher electron affinity of the 2-dehydroanilinium radical cation and uniquely efficient reaction pathways arising from the ortho relationship of the ammonio and radical site. For both the 4- and 3-dehydroanilinium radical cations, the major products in the reaction with propene were, aside from the collision-stabilized adduct ($m/z$ 135), an ammonio styrene cation ($m/z$ 120) resulting from methyl loss, and an ammonio benzyl radical cation ($m/z$ 107) resulting from ethylene loss. The relative abundances of these channels varied between the two radical cations, with the ammonio styrene cation channel preferred in the 4-dehydroanilinium reaction with propene and the ammonio benzyl radical cation channel preferred in 3-dehydroanilinium reaction with propene. This difference was explained by small energetic differences in the reaction pathway to form the ammonio benzyl radical cation, with a 2 kcal/mol difference in the rate-limiting step corresponding with an order-of-magnitude change in the state density. Despite an energetic preference towards hydrogen loss from the adduct via cyclization into an ammonio indane cation, an RRKM analysis revealed that entropic factors inhibited this channel to the point where it was not experimentally discernable from side reactions with dioxygen.

The reaction of the 2-dehydroanilinium radical cation with propene was observed to have significantly different character both experimentally and theoretically. As well as its order-
of-magnitude greater reactivity, it exhibited unique reaction pathways and products. The primary loss channel from the adduct was the likely formation of an aminotropylium ion ($m/z$ 106), via ethyl radical loss. The only other major loss channel was the formation of a methyl radical loss product ion that is likely to be 3-methylaminotropylium ($m/z$ 120). The formation of 7-membered rings is made possible by the initial adduct complex undergoing isomerization to form a more stable conventional radical cation via hydrogen transfer from the ortho-positioned protonated amino group. This isomerization channel outcompetes all other channels due to the lower energy of its rate-limiting step. The formation of 7-membered aromatic rings hints at new avenues in the formation of charged polyaromatic structures beyond conventional 6- and 5-membered rings that could be relevant to the formation of tholins in Titan’s atmosphere. Future studies on other distonic radical ions, such as protonated dehydrobenzonitrile, as well as with co-reactants like acetylene or propyne, may shed light on the importance of other such molecular weight growth pathways in reactive extraterrestrial environments.

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Supporting Information Available

Product mass spectra in the presence of additional oxygen (air) and deuteration product mass spectra for the 4- and 3-dehydroanilinium radical cations are provided along with (x, y, z) nuclei coordinates for the structures in the RRKM analysis.

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