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Direct and Indirect Hydrogen Abstraction in Cl + Alkene Reactions

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Abstract:

Reactions between Cl atoms and propene can lead to HCl formation either by direct H abstraction or through a chloropropyl addition complex. Barring stabilizing collisions, the chloropropyl radical will either decompose to reactants or form HCl and allyl products. Using velocity-map imaging to measure the quantum state and velocity of the HCl products provides a view into the reaction dynamics, which show signs of both direct and indirect reaction mechanisms. Simulated trajectories of the reaction highlight the role of the direct H-abstraction pathways and the resultant simulated scattering images show reasonable agreement with measurement. The simulations also show the importance of large excursions of the Cl atom far from equilibrium geometries within the chloropropyl complex, and these large-amplitude motions are the ultimate drivers toward HCl + allyl fragmentation. Gas-phase measurements of larger alkenes, 2-methylpropene and 2,3-dimethylbut-2-ene, show slightly different product distributions, but still feature similar reaction dynamics. The current suite of experiments offers ready extensions to liquid-phase bimolecular reactions.

Keywords: Gas-phase reaction dynamics, reactive imaging, direct dynamics simulations

1. INTRODUCTION

Reactions between chlorine atoms and alkenes occupy an important realm of atmospheric chemistry. High concentrations of chlorine atoms in the marine boundary layer and polluted coastal areas make chlorine an important player in oxidizing hydrocarbons to smaller, water-soluble species.¹ Alkenes, the reactive partner of chlorine in the current work, are an important subset of organic molecules in the troposphere. Isoprene (2-methyl-1,3-butadiene) on its own accounts for 30-50% by mass of emitted biogenic volatile organic compounds.² Degradation rates of alkenes by Cl in the troposphere can be comparable to the normally dominant OH oxidant because the reaction rate coefficients rise faster for Cl than for OH as the alkenes increase in size.¹ Alkenyl fragments, which result from hydrogen abstraction from alkenes, react with atmospheric oxygen and form long-chain enols and enones. These oxidized products, with their lower vapor pressure, are more efficient secondary organic aerosol formers than the alkenes themselves. The current work adds to the detailed description of HCl-forming reaction mechanisms between gas-phase chlorine atoms and three alkenes: propene,³⁻⁵ 2-methylpropene (isobutene),⁶ and 2,3-dimethylbut-2-ene (dimethylbutene). After ethene, propene and isobutene can be among the most prevalent alkenes in urban environments.⁷⁻⁸ The results presented here also form a bridge to recent liquid-phase studies of chlorine reactions with dimethylbutene.⁹

Reactions between chlorine and alkanes are a rich playground for exploring H-atom abstraction dynamics¹⁰⁻¹⁹ and present a convenient framework for the alkene reactions we study in the current work. Because the breaking C-H and forming H-Cl bond lengths are among the most important coordinates in the reaction, a two-dimensional potential energy surface (PES) provides remarkable insight to these reactions. This two-dimensional picture can describe direct abstractions with approach of Cl collinear to the C-H bond, which necessarily involve “rebound” reactions in which the HCl leaves with opposite velocity of the

incoming Cl atom. However, more complex descriptions of the PES are necessary to describe the dynamics appropriately for collisions with large impact parameter b in which the Cl atom travels perpendicularly to the C-H bond and the $\angle CHCl$ changes constantly. Such “stripping” reactions, another direct abstraction mechanism, can also proceed *via* the same linear C-H-Cl transition state and are common in Cl reactions with hydrocarbons.¹⁰

The reactions we study in the current work contain the same fundamental direct reaction pathways as with alkanes, but the unsaturated hydrocarbons allow the Cl atom to add to the alkene. This new reaction type, which can ultimately lead to HCl products, gives multiple stationary points and additional reaction paths that complicate the reaction dynamics. Figure 1 is a sketch of previously calculated paths on the Cl + propene PES.²⁰ The figure shows a chloropropyl addition basin and a direct reaction pathway. Braña and Sordo report no transition state leading directly from chloropropyl to HCl,²⁰ which leads to a near dead-end for the addition products. The chloropropyl radical contains about 80 kJ/mol internal energy from addition, however, and it is therefore possible for these highly excited species to form HCl and allyl products through non-intuitive mechanisms. As the reactive complex traverses the corrugated multidimensional surface, the trajectory itself leaves an imprint on the separated products. The amounts of vibrational, rotational and translational energy distributed among the allyl and HCl fragments are hallmarks of the path taken between reactants and products. One aspect of the current study uses computer simulations of reactive trajectories to provide pictures with atomic-level detail of the Cl + propene reaction.

Figure 1. Schematic reaction diagram for Cl reaction with propene. Chlorine and propene readily add to form the chloropropyl radical shown on the left basin. Direct abstractions proceed over a slight barrier on the right, encountering a small well before forming separated products. Large-amplitude motions can carry the chloropropyl complex toward products.

The chlorine-atom abstractions with propene, isobutene, and dimethylbutene, have been studied previously, but the detailed reaction mechanisms remain out of grasp. HCl-forming reactions at 298 K between Cl and propene appear to operate under differing mechanisms at high and low pressures,³ and the HCl can form vibrationally excited.⁴ Reactions between Cl and isobutene⁶ can proceed *via* long-lived complexes at low collision energy. In Cl + alkene reactions it is typical for direct abstraction to become more important as collision energy increases.²¹ Some gas-phase trends carry through to condensed-phase reactions, as in reactions between Cl and dimethylbutene,⁹ in which 25% of the nascent HCl forms in $v = 1$. It is our aim to extend and to refine the description of hydrogen abstraction by Cl from these and related alkenes.

Velocity-map ion imaging, which can measure the internal states and scattering velocities of reaction products, offers a route to detailed information about the PES that governs the reaction and the pathways of the reactive complex over it. Vibrational energy in the HCl product, for example, is a signature of extended H-Cl bond distances at the instance of H-atom transfer.²² Isotropic distributions reveal the role of long-lived reaction complexes that scramble the momentum of the reactants. Velocity distributions that peak away from 0 m/s, for example, are indicative of non-statistical reaction mechanisms.

We measure the vibrational, rotational, and velocity components of HCl produced from single collisions between Cl and alkenes using velocity-map ion imaging with state-selective multiphoton ionization of the HCl product. The present work is the first simultaneous measurement of the internal energy and velocity of either fragment in these chlorine plus alkene reactions. Direct dynamics trajectories explore the reactions in an atomic framework and show both direct and indirect reaction mechanisms. With reasonable agreement between experiment and these early calculations, we make links between the measured scattering results and the reaction mechanisms from the calculations.

II. EXPERIMENTAL APPROACH

There are three components to our gas-phase study of reaction dynamics between chlorine atoms and alkene molecules: quantum-state resolved velocity-map ion images of HCl products, REMPI spectroscopy measurement of rotational distributions of the product states, and direct dynamics calculations.

A. Velocity-Map Ion Imaging

The instrument we use to record the rotational, vibrational, and translational energy of the HCl products from Cl plus alkene reactions is the same as we have used previously for H-atom abstraction reactions by Cl.²³⁻²⁴ Two independently controlled pulsed valves form parallel molecular beams in a vacuum chamber, as shown in Figure 2. The lower, free-jet expansion of Cl₂ seeded in Ar is 17.5 mm below a skimmed molecular beam of an alkene seeded in Ar. Photolysis of Cl₂ by 355-nm light from a frequency-tripled Nd:YAG laser generates Cl atoms, some of which intersect the upper beam and react with the alkene. The mean collision energy E_{Coll} is 27 kJ/mol for propene, 31 kJ/mol for isobutene, and 36 kJ/mol for dimethylbutene. The spread in parent Cl₂ velocity dominates the uncertainty in E_{coll} , which is about 25%.²³

Figure 2. Schematic diagram of the reactive scattering instrument. Photolysis of Cl₂ in the lower molecular beam carries Cl atoms to the alkenes in the upper molecular beam.

Following state-selective ionization of HCl products, HCl cations are velocity-mapped onto a position-sensitive detector, recording the initial velocity of nascent HCl products. REMPI scans to measure HCl rotational distributions only record products that scatter in the yellow box. The center of mass moves up in the laboratory frame of reference (LAB), such that HCl with 0 m/s in the molecular frame of reference (MOL) move in the positive z direction in LAB.

The frequency-doubled output of a Nd:YAG-pumped dye laser provides tunable probe light for detecting the nascent HCl molecules. Two-photon absorption of this light is resonant with the $F^1\Delta$ state of HCl and absorbing a third photon ionizes HCl. This (2+1) resonance-enhanced multiphoton ionization (REMPI) provides quantum-state selectivity of the reaction product. Ion optics focus HCl cations on a position-sensitive detector such that the nascent velocity of the ions maps to position at the detector. A pulse of -400 V to the front face of a microchannel plate activates the detector for 100 ns, imaging those HCl products born with velocities parallel to the detection plane. A CCD camera records the arrival position of the ions as they induce a signal on a phosphor screen, and event-counting software written in LabVIEW converts each ion strike to a single-pixel event. Ionizing and detecting several thousand HCl molecules generates a contour map of the speed and direction distribution resulting from reaction between Cl and alkene for a particular quantum state. Because signals from accidental ionization of the alkene interfere with the measurement, we turn the Cl₂ photolysis laser on or off every 50 probe laser pulses to record instrument background. We present only images using this background subtraction. The reactive signals that overlap with the accidental alkene ionization remain buried under the alkene background, which reduces the sensitivity of our measurements for back-scattered HCl as we discuss below. Each image

we show is the accumulation of approximately 150 000 total laser shots taken over four hours. Data acquired many days or weeks apart are the same within the uncertainty of the measurement.

The apparatus has some non-ideal characteristics, and we consider their effects on the images. The probe laser ionizes products 1 mm above the center-line of the alkene molecule beam. This raised configuration reduces accidental ionization of the alkene, but also influences the sensitivity of the instrument. Nascent HCl molecules that back-scatter with downward velocity in the lab frame are undercounted because they must originate from reactions above the probe laser, in a less dense portion of the alkene beam. Figure 2 shows that the center of mass in the molecular frame (MOL) is moving up in the laboratory frame (LAB), somewhat alleviating the problem. A systematic study of Cl + ethane reactive scattering images as a function of probe displacement from the upper molecular beam shows a weak dependence on the resulting images.²⁵ The series of images included in the Supporting Information shows that there is little change to the detection of slow-moving LAB-frame products. A second issue arises from the finite sizes of the molecular beams and laser foci, which both allow differing transit times for the reactant Cl to intersect the alkene beam and the product HCl to reach the probe focus. Changing the time delay between the interaction of the photolysis and probe light by 6 μ s in 0.5- μ s steps compensates for these biases,²⁶ and adding the resultant images together produces the velocity-map ion images presented here.

B. Measuring Rotational Distributions of HCl Products

The distribution of internal energy in HCl can serve as hallmarks for different reaction pathways in ideal cases. The spatial separation between the forward-scattered HCl and the

background alkene signal provides a convenient route to measure the rotational distributions. We restrict the event-counting search area to the forward-scattered direction to record the HCl rotational distribution within a single vibrational manifold, with typical ranges for scattering angle of $-45^\circ < \theta < 45^\circ$ and HCl molecular-frame speeds of $300 \text{ m/s} < u_{\text{rel}} < 1000 \text{ m/s}$ as drawn in the inset of Figure 2. This restriction of the search area over-emphasizes the forward-scattered, anisotropic distribution of HCl products at the expense of isotropic or other distributions in the reactive scattering.

We use previously published correction factors²⁷⁻²⁸ for high laser intensity detection of HCl($\nu = 0$) via $F \leftarrow \leftarrow X(0,0)$ and HCl($\nu = 1$) via $F \leftarrow \leftarrow X(1,1)$ to convert measured REMPI line strengths into HCl populations. The REMPI transitions for HCl($\nu = 2$) via $F \leftarrow \leftarrow X(1,2)$ use the same resonant state as for $\nu = 1$.²⁹ Therefore, we use the $\nu = 1$ conversion factors to convert the $\nu = 2$ line strengths to population. We refer to these converted spectra as “intensity-corrected spectra” throughout the text. Using PGOPHER³⁰ to simulate the HCl intensity-corrected spectrum, we fit the rotational distribution to a single temperature T_{rot} . The spread among the two correction factors²⁷⁻²⁸ suggests an uncertainty of about 25% to the extracted rotational temperatures. We do not imply equilibrium among the HCl product rotational states, but this fitting routine provides a ready description of the energy disposal into HCl with a simple fit. We cannot make assessments of branching among vibrational levels because facile reaction between the alkenes and Cl_2 in the chamber generates background HCl, requiring changes to the experimental conditions between measuring HCl($\nu = 0$) and HCl($\nu > 0$).

C. Simulating Reactive Trajectories of Cl + Propene

Direct-dynamics simulations, in which electronic-structure calculations provide the forces acting on each atom during a trajectory, explore reactive trajectories between propene and chlorine on the atomic level. Previous calculations of the stationary points and the connecting transition states on the Cl + propene surface indicate that several bimolecular complexes are important along the direct and addition pathways.²⁰ A survey of some computational approaches shows that using the B3LYP density functional and Pople's 6-31G(d,p) basis set provides reasonable fidelity to the higher-level energies and stationary points²⁰ while decreasing computational cost.²⁵ Simulating reactive trajectories to give quantitative descriptions of the true dynamics is beyond the scope of the present work. Rather, we use their results to highlight the different types of mechanisms at play in these reactions and to provide a framework for interpreting the experimental results.

The classical trajectories use VENUS³¹⁻³² to propagate the equations of motion using forces extracted from NWChem electronic-structure calculations.³³⁻³⁴ Each trajectory starts with 27 kJ/mol of relative kinetic energy and 7 Å of separation between Cl and propene. We include the classical analogue of zero-point vibrational energy but no rotational energy in propene. Each trajectory has a predefined impact parameter b , and the set spans $0.0 \text{ Å} \leq b \leq 5.25 \text{ Å}$. During 40 trajectories with $b \geq 5.5 \text{ Å}$, the minimum distance between Cl and any H atom is 3.7 Å, and all are non-reactive. We take 5.25 Å as b_{max} for this collision energy. We use 0.3 fs or 0.5 fs time-steps and require all trajectories to conserve energy to at least 4%. About 80% of reactive trajectories conserve energy at better than 1.5%, and using this tighter tolerance on energy conservation does not change the interpretation of our results.

Analyzing the scattering velocity and internal energy of the products³⁵ allows a correlation between the atomistic simulations and the laboratory measurements. In a favorable case, the statistics offered by a large number of trajectories can reproduce the scattering images of the experiment,¹⁹ but the computational demand of the current chemical system limits our

analysis to a few-hundred reactive trajectories. Despite these limitations, the calculations still shed light on the operating reaction mechanisms.

III. RESULTS

The direct and indirect abstraction pathways of Figure 1 are both sources of HCl from propene at the collision energy we study, and similar pathways are likely in reactions with isobutene and dimethylbutene. Only the allylic hydrogens of propene are available to abstraction at our average collision energy $E_{coll} = 27$ kJ/mol. Braña and Sordo calculate²⁰ that abstracting the primary or secondary vinylic hydrogens is endoergic by more than 40 kJ/mol. Hydrogen-atom transfer among the carbon atoms in the chloropropyl addition product has calculated barriers²⁰ greater than 100 kJ/mol and does not factor in our experiment. In the current work, we consider only allylic H-atom loss from all reactants to form HCl. We use known heats of formation of propene,³⁶ allyl,³⁶ Cl,³⁷ and HCl³⁷ to determine ΔE for the propene reaction. In the absence of available data for the dimethylbutene reaction, we compute ΔE using an extrapolation to the complete-basis set limit using CBS-QB3³⁸⁻⁴¹ as implemented in Gaussian09,⁴² the same method used by Suits and co-workers for the isobutene reaction.⁶ The results appear in Table I along with some other energetic parameters, which we refer to in the Discussion.

Table I. Energetic parameters for HCl production from Cl + alkene reactions.

	Propene				Isobutene				Dimethylbutene			
	$\Delta E = -64$ kJ/mol				$\Delta E = -68$ kJ/mol				$\Delta E = -80$ kJ/mol			
HCl	T_{rot}^a	E_{avail}^b	J_{max}^{modelc}	J_{max}^{measd}	T_{rot}	E_{avail}	J_{max}^{model}	J_{max}^{meas}	T_{rot}	E_{avail}	J_{max}^{model}	J_{max}^{meas}
$v = 0$	630 ^e	5980	18	12	...	8220	19	...	...	9380	22	...

$v = 1$	200	860	14	7	210	2770	16	7	240	3520	18	7
$v = 2$	...	...	...	...	...	2	0	...	210	750	9	7

^aTemperatures in K. ^bEnergies in cm^{-1} . ^cUsing kinematic model of Ref 51. ^dEstimated as $P(J_{max}^{meas})/P_{max} = 0.1$, where P is the Boltzmann population for the assigned T_{rot} , and P_{max} is the most populated J level at T_{rot} . ^e $\text{HCl}(v = 0)$ contains a second, hotter rotational distribution as discussed in the text.

The direct H-abstraction path features a molecular complex between the nascent HCl and allyl fragments, and molecular complexes appear in the indirect abstraction channel as well. In contrast, tightly bound intermolecular structures are absent in some other well-studied H-abstraction reactions.¹⁹ In the reaction between Cl and propene, ΔE and E_{coll} combine to about 90 kJ/mol (7500 cm^{-1}). This reaction, therefore, can populate $\text{HCl}(v = 2)$ on energetic arguments, but the actual energy partitioning results from the dynamics over the potential energy surface. The reaction pathways in the alkenes we study here produce HCl in all vibrational levels up to one less than the limit predicted by the sum of ΔE and E_{coll} . Our simulations, scattering images, and rotational spectra spotlight the tangled direct and indirect hydrogen-abstraction mechanism at play in these $\text{Cl} + \text{alkene}$ reactions.

A. Insight from Trajectory Simulations

The simulations provide a starting point for interpreting the dynamics of the $\text{Cl} + \text{alkene}$ reactions. We mention in Section II that the calculations are incapable of providing quantitative descriptions of the reaction, but we show here that that we can indeed establish different reaction mechanisms that appear in the simulations. Keeping this clearer picture of

the reaction in mind, we can readily interpret the experimental Cl + alkene scattering measurements that we report in the subsequent subsections.

The approaching Cl atom can either proceed directly to HCl + allyl products, as shown by the orange arrow in Figure 1, or first move toward the chloropropyl addition complexes, as shown by the blue arrows in Figure 1. We provide a pictorial comparison of the calculated stationary points of the Cl + propene surface using previous, high-level methods²⁰ and the one we use for our trajectories in the Supporting Information.²⁵ The attractive basin in the addition pathway is slightly deeper in the trajectory calculations than in the higher levels of theory. Furthermore, transitions between the 1- and 2-chloropropyl intermediates operate through a lower barrier in the trajectory calculations. There is a transition state on the B3LYP/6-31G(d,p) surface that connects 1-chloropropyl with HCl + C₃H₅, shown schematically as the red arrow in Figure 1. The minimum-energy pathway linking these two stationary points passes near the transition state that connects 1- and 2-chloropropyl addition products to the abstraction,²⁵ suggesting that trajectories that skirt the minimum-energy pathway can blur the boundaries between the two reactive channels. Braña and Sordo do not report a corresponding transition state in their MP2 surface.²⁰ The metastable chloropropyl products in the addition channel survive many ps in our calculations, and the long lifetime of these intermediates limits our ability to simulate HCl born through long-lived complexes. The zero-point corrected ΔE for HCl + allyl is -60.7 kJ/mol in the trajectories, compared to -64 kJ/mol using tabulated heats of formation,³⁶⁻³⁷ and $\Delta H_{298K} = -60$ kJ/mol cited by Pilgrim and Taatjes.⁴

The simulations show two types of reactive trajectories. The chlorine atom abstracts an allylic hydrogen on its first encounter in about 90% of the HCl-forming trajectories we simulate. These direct abstractions follow paths similar to the orange arrow in Figure 1. The remaining 10% of reactive trajectories follow the blue arrows in the figure, interacting first with a vinyl

carbon. In these indirect reactions, the chlorine atom travels far from the center of mass of propene as indicated by the red arrow in the figure before abstracting a hydrogen atom. Even though we cannot provide completely equal treatment to simulating these long-lived complexes, the chloropropyl addition complex trajectories that we do calculate enhance our understanding of the Cl + alkene reaction dynamics. Both direct and indirect pathways are important in these reactions, but the limitations of the simulations prohibit making further assessment of the branching ratio. Among the 780 reactive trajectories in our data set, elimination of HCl from chloropropyl *via* simultaneous extension of C-Cl and C-H does not occur. We explore the intricacies of the two reaction types in the Discussion section.

We use the simulations to frame our understanding of the operating reaction mechanisms rather than make definitive predictions, and thus take a simple rather than a more sophisticated¹⁹ approach to analyzing the results of the trajectories because we can only calculate a limited number of them. The vibrational quantum number of product HCl is assigned by dividing the excess vibrational energy in the product by 2949 cm⁻¹, the calculated harmonic frequency of HCl using B3LYP/6-31G(d,p), and rounding to the nearest integer. Rotational quanta of HCl are calculated in a similar way. Most trajectories result in less than the zero-point energy in one or both products, but we cannot afford to discriminate against these quantum-mechanically forbidden trajectories. These proscribed trajectories force energy to appear in other degrees of freedom, such as in HCl rotational energy or relative kinetic energy of the products, but including them in our results is not likely to make wholesale changes to our interpretation. Figure 3 shows the calculated rotational distribution for HCl($\nu = 0$) (panel a) and HCl($\nu = 1$) (panel b) broken down by impact parameter b . As b increases, its relative importance scales as $2\pi b db$, and we use a trapezoid rule to apply this weighting for the finite sizes of b . Only 7 of 112 trajectories are reactive at $b = 5.25$ Å, and

we omit these results from further analysis because their low number makes them statistically unreliable.

Figure 3. Rotational distributions of HCl($v=0$), in panel a, and HCl($v=1$), panel b, and corresponding Boltzmann plots, panel c, from simulated Cl + propene reactions. Geometric weighting gives larger weighting to larger impact parameters b . The simulated HCl rotational distributions are hotter than the measured distributions shown in Figure 6.

Panel c of Figure 3 shows Boltzmann plots for rotational energy in $\text{HCl}(v = 0)$ and $\text{HCl}(v = 1)$. A single temperature captures the rotational energy distribution among the HCl products, with $T_{\text{rot}} = 850$ K for $\text{HCl}(v = 0)$ and $T_{\text{rot}} = 420$ K for $\text{HCl}(v = 1)$. The direct reactions figure most prominently in these extracted T_{rot} because about 90% of the reactive trajectories we simulate are from short-lived complexes. The present limitations in the simulations prevent assessments of the energy content in HCl born through long-lived complexes. The calculated distributions contain more rotational energy than in the measurements, discussed further in the Section III B and Section IV B. It is unsurprising that our calculations over-predict the rotational temperatures. Simulations of the $\text{Cl} + \text{CH}_4$ hydrogen-abstraction reaction, for example, show markedly decreased HCl rotational energy when imposing zero-point energy constraints,¹⁹ thereby giving excellent agreement with experiment. Without the luxury of an analytical potential energy surface, however, previous direct-dynamics simulations of $\text{Cl} + \text{ethane}$ that show a four-fold excess of energy in HCl rotations still describe reasonably other features of measured scattering images.⁴³

It is typical for trajectories with small impact parameters to result in back-scattered HCl and for larger b to lead to forward-scattered HCl. The top panel of Figure 4 is an unweighted plot of the scattering direction and speed of HCl from all trajectories, using the same color coding for the impact parameter as in Figure 3. Including the geometric weighting for b produces a simulated image, shown for $\text{HCl}(v = 0)$ in the bottom panel of Figure 4, in which the forward-scattered products dominate. We collect all J levels together in Figure 4 to represent scattering of direct $\text{HCl}(v = 0)$ products because the B3LYP/6-31G(d,p) surface lacks fidelity to the true surface,⁴³ as mentioned above. The rotational energy in $\text{HCl}(v = 0)$ is largely independent of scattering angle in these direct reactions. The forward-scattered $\text{HCl}(v = 0)$ have $T_{\text{rot}} = 950$ K, and back-scattered $\text{HCl}(v = 0)$ have $T_{\text{rot}} = 840$ K. Products that form $\text{HCl}(v = 1)$ scatter slightly more prominently in the forward hemisphere.²⁵

36 **Figure 4.** Scattering results from trajectory simulations. The scattering angle correlates
37 strongly with impact parameter (panel a). The simulated image (panel b), which takes into
38 account the geometric weight of b , shows strong forward-scattering of the products.

48 The simulated HCl and allyl products have available 27 kJ/mol of collision energy and 61
49 kJ/mol of zero-point corrected reaction energy, which is about 7400 cm^{-1} in total. The
50 average total kinetic energy released is about 3170 cm^{-1} for reactions forming HCl($v = 0$), and
51 both the distribution and its average are remarkably insensitive to the HCl rotational energy.²⁵
52 Most of the reactions that produce HCl($v = 1$) create allyl fragments with less than their zero-

point energy, and have similar distributions of total kinetic energy release in the $\text{HCl}(v = 0)$ and $\text{HCl}(v = 1)$ channels. The simulations show six-fold higher production of $\text{HCl}(v = 0)$ over $\text{HCl}(v = 1)$, and the limitations of our simulations prevent further assessment of the dynamics controlling the vibrational energy distribution. The direct abstraction mechanism, however, produces both ground and vibrationally excited HCl , which is a poor discriminator of the operative reaction mechanisms.⁶ With these general descriptions of the simulated scattering distributions in hand, we turn to the experimental $\text{Cl} + \text{alkene}$ scattering measurements.

B. Propene Measurements

Scattering images of $\text{HCl}(v = 1)$ from $\text{Cl} + \text{propene}$ are reminiscent of those for $\text{HCl}(v = 0)$ from $\text{Cl} + \text{alkanes}$. In both cases, the HCl is rotationally cold and the products have high relative kinetic energy. A single temperature of $T_{\text{rot}} = 200$ K fits the rotational distribution of $\text{HCl}(v = 1)$.²⁵ This temperature is only slightly warmer than $T_{\text{rot}} = 117 \pm 5$ K measured for $\text{HCl}(v = 0)$ for hydrogen abstraction from ethane⁴⁴ despite the large increase in exoergicity. Forward-scattered HCl dominates the $\text{HCl}(v = 1, J = 2-4)$ scattering image, shown in Figure 5 (panel a), which is also similar to our images of low- J HCl from $\text{Cl} + \text{neopentane}$ ²³ and other alkanes. The white circle in the figure marks the HCl speed corresponding to the maximum total kinetic energy available to the fragments given no internal excitation of the allyl fragment, $\Delta E = 55$ kJ/mol, and the average collision energy $E_{\text{coll}} = 27$ kJ/mol. Panel b of Figure 5 shows the radial distribution of the image for these scattering regions. The forward-scattering distribution reaches the energetic limit of 55 kJ/mol (4600 cm^{-1}), but also spans a broad range. Thus, there are some reactions that deposit very little energy in the internal modes of the allyl fragment and others deposit much more. Uncertainty in one or both of the experimental collision energy and calculated exoergicity of the reaction permit the distribution to extend beyond the indicated cutoff. The angular distribution (panel c of Figure

5) and rotational distributions²⁵ of $\text{HCl}(v = 1)$ point toward a stripping-type mechanism similar to the dominant mechanism in alkane reactions.¹⁰ The broad translational energy distributions, however, indicate that a slightly more complicated mechanism may be at play in the alkene reactions.

Figure 5. Measured $\text{HCl}(v = 1, J = 2-4)$ distributions from Cl reaction with propene. The image shows that products scatter forward (panel a) and reach the predicted energetic limit shown by the white circle in the image and black line in the product radial distribution (panel b). The speed-dependent angular distributions (panel c) show forward and side scattering.

The reaction produces $\text{HCl}(v = 0)$ with two distinct rotational distributions, as shown by the measured spectrum in Figure 6 (panel a) and the corresponding Boltzmann plot in panel b, which indicates two reaction mechanisms lead to HCl formation. Fitting the intensity-corrected spectrum (black line) to the lowest 6 HCl rotational states gives $T_{rot} = 630$ K, with the simulated spectrum³⁰ shown in blue. The Boltzmann plot shown in panel b is a simplified version of more complete analysis described in the Supporting Information.²⁵ Disparate energy distributions within a single product can be signatures of multiple reaction pathways. This measurement, however, is not a direct assessment of the branching between these pathways. Our experiment overemphasizes the forward-scattered products in determining the rotational populations because we choose a search area that minimizes background signal, as described in Sec. II B. The rotationally cold distribution in $\text{HCl}(v = 0)$ is consistent with a stripping mechanism as in $\text{HCl}(v = 1)$ and the trajectory calculations support direct reactions producing HCl in both vibrational states. The rotationally hot distribution, on the other hand, could result from longer-lived complexes that can facilitate energy partitioning among products.

Figure 6. Measured rotational distributions of HCl from Cl reactions with propene and dimethylbutene. The HCl($v=0$) products from reactions with propene (panels a and b) show

two rotational distributions that are indicative of two operative mechanisms: a cold distribution with $T_{rot} = 630$ K, and a hotter distribution ill-described by a temperature. Panel b shows the Boltzmann distribution of the spectrum in panel a; complete details of the fit are available in the Supporting Information.²⁵ HCl($v = 1$) products (panel c) from dimethylbutene reactions have a similar rotational energy to the HCl($v = 2$) products (panel d). The measured peak intensities have been corrected by scaling factors as described further in the Supporting Information.

The HCl($v = 2$) channel is only just accessible at our collision energy. It represents a minor pathway at most and leaves only a few hundred cm^{-1} of energy for relative kinetic energy and internal excitation of products. In stripping reactions, it is typical for the kinetic energy of the reaction to appear as relative kinetic energy rather than in the internal modes of the products.¹⁰ Similar dynamics in stripping reactions in alkenes predict minimal flux into HCl($v = 2$) production. We detect, at best, one weak transition at HCl($v = 2, J = 1$) for the Cl + propene reaction.

C. Isobutene Measurements

Methylpropene (isobutene) is only slightly more chemically complex than propene and provides a systematic route to studying increasingly complex hydrogen-abstraction reactions. State-resolved scattering provides an interesting overlap with similar ion-imaging results that detect the isobutenyl radical irrespective of its internal energy.⁶ Allyl hydrogen abstraction from isobutene⁶ is exoergic by 68 kJ/mol, and isobutenyl + HCl($v = 2$) is approximately isoenergetic with the reactants. Flux to the HCl($v = 2$) channel is insufficient for our imaging

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3 measurement and we detect only the lowest rotational states of $\text{HCl}(v = 2)$. Unintended
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5 reactions in the vacuum chamber between Cl_2 and the alkene lead to incomplete removal of
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7 background HCl signals that overwhelm reactive $\text{HCl}(v = 0)$ production. We only analyze
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9 $\text{HCl}(v = 1)$ for the reaction of Cl with isobutene, but expect $\text{HCl}(v = 0)$ production is still a
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11 major pathway and contains similar features to the $\text{Cl} + \text{propene}$ results.
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14 A single temperature, 210 K, captures the $\text{HCl}(v = 1)$ distribution from this reaction.²⁵ The
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16 increases in exoergicity and collision energy in this reaction compared to that with propene,
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18 as listed in Table I, lead to similar measured rotational temperatures for $\text{HCl}(v = 1)$. The
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20 reactive scattering image in Figure 7 (panel a) of $\text{HCl}(v = 1, J = 2-4)$ shows that products
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22 scatter more prominently in the forward direction for isobutene than propene reactions. The
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24 distribution does not approach the energetic limit, marked by the white ring in the image and
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26 the black vertical bar in the radial distributions of panel b of the figure. These radial
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28 distributions show that nearly all reactions leave the isobutenyl fragment internally excited.
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30 The angular distributions, shown in panel c, show little side-scattering in the products.
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Figure 7. Measured HCl($v = 1, J = 2-4$) distributions from Cl reaction with isobutene. The image shows that products scatter forward (panel a) but fail to reach the predicted energetic limit shown by the white circle in the image and black line in the product radial distribution (panel b). The angular distributions (panel c) show less side scattering than in propene.

The distribution of products away from 0 kJ/mol scattering energy is similar to the results from Suits and co-workers,⁶ who detect the isobutenyl fragment independent of its quantum state. This previous work,⁶ however, shows a stronger isotropic component of the scattering.

The scattering image we present in Figure 7 is for a particular subset of HCl products, and we argue below that the image and the HCl rotational distribution²⁵ for HCl($v = 1$) are consistent with stripping mechanisms that favor forward-scattered products.¹⁰ It is possible that the discrepancy between previous⁶ and our current scattering images result from the differences in product detection.

D. Dimethylbutene Measurements

Complete substitution of the vinyl hydrogen atoms for methyl groups on isobutene gives 2,3-dimethylbut-2-ene (dimethylbutene). Removing any of the twelve hydrogen atoms creates a very stable dimethylbutenyl radical, with a best estimate of $\Delta E = -80$ kJ/mol. This large energy change provides a route to producing a quantifiable HCl($v = 2$) distribution. Our group has recently shown that hydrogen abstraction by Cl from dimethylbutene in the condensed phase produces vibrationally excited HCl,⁹ and the current work seeks to provide a detailed, gas-phase picture of the reaction. Because contaminant HCl hampers our ability to measure reactive HCl($v = 0$), as in isobutene, we only analyze HCl($v = 1$) and HCl($v = 2$) for this reaction. As in isobutene reactions, we expect Cl + dimethylbutene to produce HCl($v = 0$) as a major reaction pathway.

Panel c of Figure 6 shows the intensity-corrected rotational spectrum (black line) of HCl($v = 1$) from Cl + dimethylbutene with the simulated (blue line) $T_{rot} = 240$ K, and panel d of the figure shows the spectrum for HCl($v = 2$) with $T_{rot} = 210$ K. The scattering image in Figure 8 (panel a) shows that, as in reaction with isobutene, the polyatomic radical is internally excited. The radial distribution of forward-scattered products, shown in panel b of the figure, has a maximum about 7 kJ/mol higher than in isobutene. There is an extra 5 kJ/mol of collision energy and 12 kJ/mol from ΔE in dimethylbutene reactions relative to isobutene,

and about 50% of this excess energy appears in product translation. The distributions also show that many reactions have little kinetic energy released in the products, leaving more than 40 kJ/mol in the dimethylbutenyl fragment. As the alkene increases in size, the fraction of energy deposited in the polyatomic fragment increases, a trend that is consistent among Cl reactions with ethane,⁴⁵ butane,⁴⁶ and neopentane.²³ The hotter HCl rotational temperature and population of higher vibrational states in the dimethylbutene reaction, however, indicates that some of the ΔE of reaction appears in the internal degrees of freedom of the products. The angular distributions, in panel c of Figure 8, are similar to those of isobutene and show predominantly forward-scattered products. The HCl($v = 2$) products are rotationally cold, shown in panel c of Figure 6, and have forward-scattered products, which point to stripping dynamics in this reaction pathway as well.

HCl($v = 1, J = 2-4$) from Cl + Dimethylbutene

Figure 8. Measured HCl($v = 1, J = 2-4$) distributions from Cl reaction with dimethylbutene.

The image shows that products scatter forward (panel a) and, as in reaction with isobutene, fail to reach the predicted energetic limit shown by the white circle in the image and black line in the product radial distribution (panel b). The angular distributions (panel c) are similar to isobutene reactions.

IV. DISCUSSION

Previous studies of the vibrational energy content in HCl from Cl + propene ascribed the varying energy disposal to two different reaction mechanisms.^{4, 47} We have shown in Sec. III that rotationally cold distributions of HCl appear for both the $\nu = 0$ and $\nu = 1$ manifolds. These two distributions are similar to the direct-abstraction mechanism invoked in Cl + alkane reactions.¹⁰ The distributions seem to show that the vibrational energy content of HCl fails to be the key indicator of the reaction mechanism, as mentioned in previous work.⁶ The two rotational distributions of HCl($\nu = 0$) do, however, herald a pair of operative reaction mechanisms at our single-collision conditions. At 0 Torr ambient pressure,³ the Cl + propene reaction features 2:1 branching between a pressure-independent mechanism and a pressure-dependent one.⁴⁸ These two mechanisms³ are consistent with direct and complex-mediated reactions, which we untangle through careful examination of our simulations and experimental results.

A. Reaction Types in Simulations

We reiterate that the simulations are incapable of providing exact descriptions of the reaction dynamics at work in these Cl + alkene reactions. They are useful, however, in highlighting certain types of reaction paths that can be important, and we show four different hydrogen-abstraction mechanisms from the Cl + propene simulations. For many collisions with large impact parameter, b greater than about 4 Å, an allylic hydrogen atom transfers to the Cl atom as it passes, with small deflections to the Cl velocity. Panel a of Figure 9 shows a representative path of the Cl atom (or HCl center of mass after H-atom transfer) relative to a fixed propene coordinate system for one such reaction.⁴⁹ In these “stripping” reactions, the HCl can form vibrationally excited if the H transfers to the Cl at H-Cl distances greater than its equilibrium bond length. The simulations show that reactive trajectories with larger impact parameters tend to short-cut the minimum-energy path, depositing energy into the newly

forming H-Cl bond.²⁵ Because collisions with large b are geometrically more likely than small b , these reactions dominate the reaction cross section, leading to the forward-scattered distributions in Figures 3 and 4.

Figure 9. Cartoon representation of four simulated reactive trajectories. In direct abstractions, collisions with large impact parameter (panel a, File: Stripping.xyz) lead to forward scattering, and collisions with small impact parameter (panel b, File: Rebound.xyz) lead to back scattering. Reactive trajectories that proceed through addition complexes (panel c, File: Addition.xyz) have large-amplitude motions of Cl before abstracting an H atom from the CH₃ end of propene. Dynamics in the exit-channel complex can have a marked effect on the internal energy of the products (panel d, File: ExitComplex.xyz), in this case a second interaction imparts an additional two quanta of vibrational energy in HCl. Trajectories available as Supporting Information.

Direct reactions from head-on collisions, with b less than about 2 Å, result in backwards-scattered products. Most of these trajectories stay close to the minimum-energy path, which reduces the average HCl vibrational content.²⁵ In many cases, the system proceeds smoothly to products, giving a direct reaction that is similar to the direct reactions at large b but with contrary scattering. One back-scattering reactive trajectory is sketched in Figure 9 (panel b) for $b = 1.0$ Å.⁴⁹

Some of the trajectories have more mercurial behavior at the point of hydrogen-atom transfer. Examination of these trajectories shows that in these “chattering” reactions,^{14, 43, 50} Cl first encounters the H atom in a non-linear $\angle CHCl$, and the system cannot turn the corner to the products and instead rebounds off the repulsive wall. If, as the Cl retreats from propene the system reaches a nearly linear geometry, the H atom can transfer to Cl. This class of trajectory appears for all impact parameters we study. Limited numbers of trajectories and background noise in the experiment prevent further analysis of the differences between these two kinds of back-scattering reactions.

The Cl interacts with the carbon chain of propene before abstracting H in approximately 10% of the reactive simulated trajectories. In these reactions, the 1-chloropropyl and 2-chloropropyl intermediates have about 100 kJ/mol of internal energy. The chlorine atom can readily shift between the 1- and 2-carbon positions *via* a transition state that is about 75 kJ/mol less than the available energy,²⁵ resulting in a highly fluxional addition complex. There is a transition state that connects the addition and direct reaction pathways on the B3LYP surface that we use to propagate trajectories, and this minimum energy pathway provides a direct connection to HCl products.

The electronic structure calculations do not support ejection of HCl from chloropropyl through concomitant C-Cl and C-H bond extension. Our trajectories are too computationally expensive to simulate effectively long-lived complexes that might eventually exhibit these

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3 dynamics. The current set of reactive trajectories instead highlights the importance of the
4 large-amplitude motions of Cl atoms in the metastable chloropropyl radical. In one example,
5 shown in panel c of Figure 9, the Cl atom first approaches the 1-carbon, orbits around
6 propene about 4 Å away from the carbon chain and only 30° above the C-C-C plane, and
7 extracts the H atom when external to propene.
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12 Although a transition state connects the two reaction paths, this trajectory shows that the
13 dynamics of the reaction can carry the reactive complex on very different paths *en route* to
14 HCl and allyl products.⁴⁹ In the absence of stabilizing collisions, the chloropropyl fragment
15 must keep its E_{coll} of 27 kJ/mol above its dissociation threshold to Cl + propene. If this extra
16 energy appears in the appropriate degrees of freedom, the complex can eject the Cl atom.
17 Prior to its departure, however, the Cl can take large excursions around the propene fragment
18 and then leave with a very different angle and speed compared to its entry. These large-
19 amplitude motions are similar to those that operate in the roaming reactions of certain
20 unimolecular dissociation reactions.^{19, 51-52} In the case of the Cl + alkene reactions we study,
21 if these large-amplitude motions within the addition complex take the Cl atom near the CH₃
22 end of the molecule, it can abstract a hydrogen atom.
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39 Irrespective of the route to HCl and allyl, the nascent products continue to interact as they
40 separate. The exit-channel complex, in which the HCl molecule points at the de-localized π
41 orbital of allyl, lies about 14 kJ/mol lower in energy than fully separated products.
42 Anisotropic forces on the HCl moiety during separation change the energy content between
43 its initial formation and complete separation. In one extreme example, shown in Figure 9
44 (panel d), the initial momentum of Cl carries the nascent HCl across the length of the co-
45 fragment.⁴⁹ Because the two CH₂ ends of the allyl fragment are equivalent following H
46 abstraction, the H atom can partially bond with the *other* end of the allyl fragment while the
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Cl continues to move away. In this strange case, traversing the exit channel imparts about 5000 cm⁻¹ of additional vibrational energy into the HCl molecule.

B. Energy Disposal into Products

Direct reactions, as in HCl production from Cl + alkanes, can lead to large kinetic energy releases and forward scattered products.¹⁰ Our direct-dynamics simulations and reactive scattering images of HCl($v \geq 1$) for the propene, isobutene, and dimethylbutene reactions are all consistent with this picture. The measured Cl + propene scattering image of HCl($v = 1$, $J = 2-4$) in Figure 5, for example, detects direct-reaction products because the HCl($v = 1$) distribution contains only a cold T_{rot} as in Cl + alkane reactions.¹⁰ The direct-dynamics simulations also emphasize the direct hydrogen-abstraction pathways because the indirect reactions take too long to simulate effectively. We take the set of simulated HCl($v = 0$, $J < 20$) products in Figure 4 (panel b) as a representative comparison to the direct-abstraction scattering image of Figure 5 in the absence of sufficient trajectories. Both simulated and measured images show products that scatter forward and with lots of total relative kinetic energy.²⁵

Our ability to explicitly correlate the hot rotational distribution of HCl($v = 0$) with the indirect reactions is hampered by the exceedingly long lifetimes of the chloropropyl radicals and the low flux into any one HCl state with $J \gtrsim 6$. The simulations show a continuum of chloropropyl lifetimes prior to reaction, indicating that drawing a distinct dividing line between these two reaction mechanisms may be difficult. Approximately 30% of the trajectories are stuck in reaction complexes after about 3 ps of simulation time, and we do not propagate these trajectories further. In the experiment, however, the chloropropyl radical must decay either to HCl + allyl or back to reactants. Further trajectory calculations that use

a more accurate PES and can simulate many more Cl + propene collisions will help provide a more definitive experimental handle on the indirect pathways.

Deposition of rotational energy in HCl shows good agreement with the kinematic model of Valentini and co-workers for hydrogen abstractions in Cl + CH₄ and Cl + C₂H₆ reactions,⁵³ and we examine its ability to describe Cl + alkene reactions. This model uses ΔE , E_{coll} , and the masses of the interacting particles to predict the appearance of energy in different modes of HCl, yet it ignores the specifics of the potential energy surface and its forces on the reactive complex. Because the rotationally cold distribution in the HCl($v = 0$) and HCl($v = 1$) channels of Cl + propene result from direct reaction paths, we can apply the same treatment to the current system. In this way, the kinematic model⁵³ predicts the highest populated rotational level $J_{max}^{model} = 18$ for HCl($v = 0$) and $J_{max}^{model} = 14$ for HCl($v = 1$), as listed in Table I, slightly higher than our (estimated) measured values of $J_{max}^{meas} = 12$ for HCl($v = 0$) and $J_{max}^{meas} = 7$ for HCl($v = 1$). The model readily accounts for the difference of HCl rotational energy from direct reactions between the two vibrational levels despite overestimating J_{max} . The kinematic model⁵³ drastically over predicts J_{max} for isobutene and dimethylbutene reactions, also listed in Table I. The scattering images in Figures 5, 7, and 8 show that the larger isobutenyl and dimethylbutenyl fragments receive much more excitation than the allyl fragment, but the model explicitly prohibits energy deposition into the polyatomic co-fragments. It is therefore less likely to apply directly in reactions with these larger alkenes, and this omission in the model shows that the dynamics of the larger polyatomic fragment are important to the ultimate understanding of the Cl + alkene system.

C. Trends among Propene, Isobutene, and Dimethylbutene Reactions

The larger alkenes have more stable alkenyl radicals, more vibrational modes, and exhibit more anisotropic product scattering with lower total kinetic energy released. Increasing the number of methyl substituents to the double bond stabilizes the alkenyl radical product, increasing the exoergicity for H abstraction by Cl from -64 kJ/mol in propene to -80 kJ/mol in dimethylbutene. We detect HCl with vibrational energy up to the limit predicted by ΔE with zero collision energy. The collision energy is not a variable parameter in our experiment, so we cannot determine its role in controlling the energy distributions. Previous work, however, determined that vibrationally excited HCl from propene is an important pathway at only a few kJ/mol collision energy.⁴ These results suggest that similar trends hold in the alkene reactions as in with alkanes: ΔE is more important than E_{Coll} in promoting vibrationally excited HCl products

The fractional kinetic energy released in the products decreases with increasing alkene size. Alkane reactions with Cl also show similar behavior,^{23, 45-46} but the trend is stronger in the alkenes. The Cl + propene products reach their kinetic energetic limit for HCl($\nu = 1, J = 2-4$), but the dimethylbutene products fall about 40 kJ/mol (3340 cm^{-1}) short. There are more vibrational modes in dimethylbutene than in propene, which could lead to more efficient energy transfer during the collision and therefore less kinetic energy in the products. Reorganization of the polyatomic structure, which changes from localized to delocalized π bonding, is another route to internal excitation of the polyatomic fragment. It is also possible that in Cl + dimethylbutene collisions, more rotational energy can transfer into the polyatomic fragment. Without further calculations or additional imaging experiments, we do not make a definitive assessment of which modes soak up the undetected energy.

D. Comparison to Liquid-Phase Reactions

We have previously studied HCl formation in chlorine-atom reactions with dimethylbutene in the condensed phase with ps time resolution.⁹ In these reactions, diffusion of the Cl atom through the solvent controls the appearance of HCl.¹⁸ The proximity of solvent molecules will likely inhibit the requisite large-amplitude motions of the Cl atoms in the crossover reactions. Furthermore, the solvent will quickly remove vibrational energy from chlorine addition products, effectively trapping the intermediates. Direct, either stripping or rebound, abstractions will be the only major source of HCl in the condensed phase, and they produce vibrationally excited HCl about 25% of the time.⁹

Dimethylbutene reactions in chlorinated solvents produce both HCl($\nu = 0$) and HCl($\nu = 1$). The current work is the first measurement to show that HCl($\nu = 2$) forms in gas-phase reactions between Cl and dimethylbutene. The condensed-phase reactions, however, do not produce measureable amounts of HCl($\nu = 2$).⁹ Among the reactions we have studied, there is a growing trend for molecular products to have less vibrational excitation in the liquid-phase analogues of the gas-phase reactions.^{9, 54-55} The solvent can control the energetics of the reaction by preferentially solvating the reactants over the products, for example, limiting the energy available for vibration. The solvent continually buffets the system and can remove energy from the reactive complex even as the products are forming. This solvent friction can inhibit the conversion of potential energy of reactants into vibrational energy as the system leaves the transition state. In addition, molecular complexes in the exit channels of these alkene reactions offer another opportunity for energy loss to the solvent.

The solvent itself forms an integral part of the condensed-phase reactions in many cases, such that making analogies to gas-phase reactions is only the first step to understanding liquid-phase reactions. The reacting liquid-phase radical is often not “bare,” for example, but rather a radical-solvent⁵⁶ or radical-co-radical⁵⁷⁻⁵⁸ complex. Thus, it is possible that these complexes modify the transition state in a way that has little analogue to the gas phase. Contrasting the

gas- and liquid-phase outcomes of exothermic reactions that form vibrationally excited products is providing new opportunities to quantify the importance of all these, and related, liquid-phase effects.⁵⁹ However, for a full interpretation of the liquid-phase dynamics, the bare dynamics must be first benchmarked by experiments and theory of the type we present here under isolated, gas-phase conditions.

V. CONCLUSION

Gas-phase velocity-map ion imaging and direct-dynamics simulations of chlorine reactions with propene, 2-methylbutene (isobutene), and 2,3-dimethylbut-2-ene determine the hydrogen-abstraction mechanisms and their resultant product distributions. Forward-scattered vibrationally excited HCl, in which its velocity is little changed from the initial velocity of the Cl atom reactant, dominates the images at our collision energies near 30 kJ/mol. The exoergicity of these reactions, which result from the relative stability of the alkenyl products, permits formation of vibrationally excited HCl. All reactants show rotationally cold distributions of HCl($v = 1$). These reactant distributions are consistent with stripping-type mechanisms that operate in Cl reactions with alkanes.¹⁰

Two HCl rotational distributions, one cold and one hot, in the HCl($v = 0$) manifold of the Cl + propene reaction signal two competing reaction mechanisms. There are also two reaction mechanisms in direct-dynamics simulations: direct and indirect hydrogen abstraction. Hydrogen quickly transfers to Cl in direct reactions, leading to rotationally cold HCl. Chlorine first adds to the C=C bond in indirect reactions, forming the 1-chloropropyl and 2-chloropropyl addition complexes. In these indirect reactions, the Cl experiences large excursions from chloropropyl equilibrium geometries before abstracting a hydrogen atom.

These two mechanisms are candidates for the two $\text{HCl}(v = 0)$ rotational distributions, but further simulations can help link the HCl rotational energy content to each mechanism.

The present gas-phase results are in concert with our previous condensed-phase studies⁹ of chlorine atoms abstracting hydrogen from dimethylbutene in liquid CDCl_3 . Because the surrounding solvent inhibits the large-amplitude motions necessary to cross from the addition to direct reaction channels, only direct abstractions form HCl . In these direct hydrogen abstractions at thermal collision energies of about 3 kJ/mol, products branch to 25% $\text{HCl}(v = 1)$ and 75% $\text{HCl}(v = 0)$.⁹ Many features of the gas-phase reaction dynamics are still important in liquids, but the constant interaction with the solvent closes some of the available pathways.

Supporting Information Available: The supporting information contains a further analysis of the instrumental bias and HCl rotational distributions, additional details of the $\text{Cl} +$ propene simulation results, and the four trajectories mentioned in the text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Table of Contents Image

To addition
complexes

Direct Reaction

a) HCl($v = 0$)

b) HCl($v = 1$)

c) Boltzmann Plot of Simulated HCl Product States

1
 2
 3
 4
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 29

a)

Simulated HCl($v = 0$) Image

b)

Scattering Image

Product Radial Distribution

Scattering Angle, θ

0° - 60°

60° - 120°

120° - 180°

Energetic
Limit

Total Kinetic Energy Release / kJ/mol

Product Angular Distribution

Scattering Speed, u_{cm}

390 - 700 m/s

700 - 1010 m/s

1010 - 1325 m/s

ACS Paragon Plus Environment

Scattering Angle, θ / Degree