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The dynamics of the $CI+n-C_4H_{10}\rightarrow HCI(v',j')+C_4H_9$ reaction at 0.32 eV

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Rotational state resolved center-of-mass angular scattering and kinetic energy release distributions have been determined for the HCl (v'=0, j'=0-6) products of the reaction of chlorine with *n*-butane using the photon-initiated reaction technique, coupled with velocity-map ion imaging. The angular and kinetic energy release distributions derived from the ion images are very similar to those obtained previously for the Cl plus ethane reaction. The angular distributions are found to shift from forward scattering to more isotropic scattering with increasing HCl rotational excitation. The kinetic energy release distributions indicate that around 30% of the available energy is channeled into internal excitation of the butyl radical products. The data analysis also suggests that H-atom abstraction takes place from both primary and secondary carbon atom sites, with the primary site producing rotationally cold, forward scattered HCl(v'=0) products, and the secondary site yielding more isotropically scattered HCl(v'=0) possessing higher rotational excitation. The mechanisms leading to these two product channels are discussed in the light of the present findings, and in comparison with studies of other Cl plus alkane reactions. (© 2004 American Institute of Physics. [DOI: 10.1063/1.1792593]

I. INTRODUCTION

A key feature of the reactions of chlorine atoms with alkanes containing more than two carbon atoms is the availability of several reaction pathways, namely, abstraction of a hydrogen atom from a primary, secondary, or tertiary carbon atom. It is therefore of interest to investigate the reactivities of these sites, and the reaction dynamics associated with the different chemical channels. The reaction of atomic chlorine with *n*-butane $(n-C_4H_{10})$ can proceed via two pathways:

$$Cl+n-C_{4}H_{10} \rightarrow HCl+CH_{2}CH_{2}CH_{2}CH_{3}$$

$$\Delta_{r}H_{0}^{\theta} = -8.4 \pm 2.1 \text{ kJ mol}^{-1}, \qquad (1)$$

$$\rightarrow HCl+CH_{3}CHCH_{2}CH_{3}$$

$$\Delta_{r}H_{0}^{\theta} = -23.1 \pm 2.1 \text{ kJ mol}^{-1}. \qquad (2)$$

The different exothermicities¹⁻⁴ of reactions (1) and (2) suggest that the dynamics of the competing pathways may be investigated by quantum state selective measurements of the scattering of the HCl (v', j') products.

There have been numerous kinetic studies of the reaction of chlorine atoms with *n*-butane.⁵⁻¹⁷ The recommended value of the absolute rate coefficient is (2.05 ± 0.07) $\times10^{-10}$ cm³ molecule⁻¹ s⁻¹, independent of temperature over the range 290–600 K.¹⁸ In recent relative rate experiments using gas chromatographic product analysis, Sarzynski and Sztuba found a weak negative temperature dependence for abstraction of H atoms from a primary carbon atom, and a weak positive temperature dependence for abstraction from a secondary carbon atom over the temperature range of 295–470 K.¹⁷ The different behavior was proposed to arise from the formation of a weakly bound complex during abstraction of a secondary H atom. A preference for abstraction of an H atom from secondary carbon atoms over primary carbon atoms was observed in the relative rate experiments carried out by Tyndall *et al.*¹⁴ and Sarzynski and Sztuba.¹⁷ In both experiments, 29% of the butyl products were found to result from abstraction of a primary H atom, and 71% from abstraction of a secondary H atom.

In contrast to the kinetic work, to date the dynamics of the two reactive pathways have not been examined. *Ab initio* calculations on the transition state geometries of the Cl plus propane and Br plus propane and *n*-butane reactions at both primary and secondary carbon sites show a near collinear *X*-H-C arrangement (where *X* is Br or Cl),^{19,20} suggesting that the Cl plus *n*-butane reaction is likely also to be characterized by a near-linear transition state. By virtue of this, the dynamics of abstraction of a primary (and possibly secondary) H-atom from *n*-butane are anticipated to be similar to those for H-atom abstraction from ethane.²¹

At collision energies ≤ 0.5 eV, the HCl products of the abstraction reactions of Cl with a variety of alkanes are found predominantly in the ground vibrational state and are rotationally cold.^{22–26} The products of abstraction from a secondary or tertiary carbon atom are generally more rotationally excited than those formed by abstraction from a primary carbon site.^{23–26} Abstraction from secondary and tertiary carbon atoms is found to be favored by a factor of 2–3

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over the statistical ratio of primary to secondary or tertiary atoms.²³⁻²⁶

Photon initiated (photoloc) experiments²⁴⁻²⁶ on a variety of Cl plus alkane reactions have tended to assume that the systems may be approximated to three-body reactions, implying that internal modes of the alkyl fragments are not excited. Within this approximation, the products of abstraction from primary carbon sites are seen to be more forward scattered than the products of abstraction from secondary or tertiary sites. Suits and co-workers have studied the reactions of chlorine with propane²⁷ and *n*-pentane²⁸ at a series of collision energies using a crossed molecular beam apparatus. In the former case the scattered propyl radical products were detected using 9.5 eV vacuum ultraviolet synchrotron radiation coupled with quadrupole TOF mass spectrometry of the resulting ions. The center-of-mass (c.m.) angular scattering distribution was seen to be nearly isotropic, with a peak in the forwards direction and a smaller peak in the backwards direction. The propyl products were found to be more forward and sideways scattered with increasing collision energy. Interestingly, these studies also suggest that, at the lowest collision energy, 40%-50% of the available energy is partitioned into the internal degrees of freedom of the products.^{27,28} Based on the low rovibrational excitation observed by Varley and Dagdigian in the HCl products of the Cl plus propane reaction at a similar collision energy,²⁵ it was concluded that most of the available energy must be channeled into internal modes of the propyl radical products, and therefore that these fragments cannot be considered as spectators in the reaction.^{27,28}

The Cl plus *n*-butane reaction has recently been studied at 0.32 eV by Toomes and Kitsopoulos using an unskimmed crossed beam technique.²⁹ Angular scattering distributions were extracted from the returned images by direct integration of the raw data over velocity. Unlike forward convolution methods, this approach does not take into account the differing sensitivities to forward and backward scattered products or the speed distribution of the Cl atoms. Differentiation between the two available reaction pathways was thus not possible. The HCl (v'=0, j'=1-4) products were found to be predominantly forward scattered, while the HCl (v'=0, j'=5) products were more isotropically scattered. The scattering dynamics observed for the Cl plus butane reaction were found to be very similar to that for Cl plus ethane. Given this fact, coupled with the results of earlier work by Varley and Dagdigian,²⁴⁻²⁶ which indicated that both primary and secondary or tertiary hydrogen abstraction processes contribute to most of the product HCl/DCl rotational states, it was concluded that the primary or secondary nature of the H atom abstracted exerts little influence over the scattering dynamics in the Cl plus *n*-butane reaction.²⁹

In the following paper, we describe the results of a photoloc study of the title reaction in which the HCl products have been probed by velocity map ion imaging. The experimental work, performed in Crete and described in Sec. II A, uses the same apparatus as that employed in our earlier study of the Cl plus ethane reaction.²¹ In that work, velocity-map ion images of the HCl products of the photon-initiated reaction were analyzed using a moment expansion method which allows determination of both the c.m. angular scattering and kinetic energy release distributions of the products. The similar analytical procedures employed here, described briefly in Sec. II B, allow determination of the HCl rotational quantum state resolved differential cross-sections, the internal excitation in the butyl coproducts, and the relative reactivity of the *n*-butane to primary and secondary H atom abstraction. These results are presented in Sec. III, while in Sec. IV and V we discuss our findings in the context of previous work on the Cl plus alkane reactions, and present our final conclusions.

II. METHOD

A. Experimental procedures

The experiments were performed using the ion imaging apparatus at the Institute for Electronic Structure and Laser in Crete, which has been described in detail elsewhere.^{30,31} A 1:1 mixture of Cl_2 and *n*-butane stored in a glass bulb at a backing pressure of ~600 Torr was coexpanded in a pulsed molecular beam using a homemade piezoelectric nozzle with a 1 mm orifice operating at 10 Hz. Standard velocity-mapping ion optics³² were mounted directly in front of the nozzle, with the nozzle and the repeller plate maintained at the same voltage to avoid electrical discharging during the gas pulse.

Midway between the repeller and extractor plates the molecular beam was intersected at right angles by the counter-propagating radiation from two lasers. Photolysis of Cl₂ at 355 nm using the third harmonic output of a Nd: (YAG) laser (~20 mJ per pulse) afforded nearly monoenergetic ground state $Cl(^{2}P_{3/2})$ atoms traveling at 1675 ms⁻¹. Assuming that the relative motion between the molecular chlorine precursor and butane is small, due to efficient translational cooling in the jet expansion, the photolysis defines the relative motion of the chlorine atom and the butane molecule, yielding a mean collision energy of 0.32 eV with a full width at half maximum of 0.06 eV. The spread is due to residual thermal motion of the precursor and reagent, and was calculated using an estimated translational temperature of 50 K, based on probe-only images of background HCl (Ref. 33) (see below).

The HCl (v'=0) products were detected with rotational state-resolution via (2+1) resonantly enhanced multi photon ionization (REMPI), either through the Q branch of the $E(^{1}\Sigma^{+})$ state³⁴⁻³⁶ for j'=0-5, or through the *R* branch of the $F({}^{1}\Delta_{2})$ state³⁴⁻³⁶ for j' = 1, 3 and 6. The probe radiation was generated using the frequency-doubled output of a Nd:YAG pumped optical parametric oscillator (Spectra-Physics Pro 250, MOPO) with a typical pulse energy of ~ 1 mJ. For each transition the probe laser was scanned over the Doppler profile of the HCl product. Both photolysis and probe laser beams were linearly polarized in the plane of the detector and were focused using 25 cm focal length lenses. The timing of the experiment was controlled using digital delay pulse generators (SRS DG535). A short delay of between 120 and 150 ns between the photolysis and probe laser pulses allowed sufficient HCl product density to build up prior to detection. Due to the narrow focus of both laser beams, care was taken to ensure that fly-out was avoided (see Sec. III). Suitable electrostatic potentials applied to the repeller and extractor plates of the ion optics effected velocity mapping³² of the ionized reaction products onto the detector [a pair of matched MCPs (Hamamatsu) coupled to a *P*46 phosphor anode (Proxitronic)]. $H^{35}Cl^+$ ions were detected mass selectively by pulsing the voltage applied to the MCPs from -1100 V to -1600 V at the appropriate time of flight. The resulting images were captured using a charge coupled device camera (Cohu 4910) and sent to a PC for signal averaging (EYESPY Software by *k*-Space Associates).

As discussed previously,²¹ velocity calibration of the ion images was achieved by direct detection of the Cl $({}^{2}P_{3/2})$ photofragments from Cl₂ photolysis at 355 nm via the $4p {}^{4}P_{3/2} \leftarrow {}^{2}P_{3/2}$ transition at 240.46 nm.³⁷ Cl images were obtained under similar time-delay and molecular beam intensity conditions to those used for the studies of the Cl plus ethane and Cl plus butane bimolecular reactions. The radial coordinate of the resulting images could be transformed directly into velocity using the known single velocity of the Cl photofragment.^{38,39} Direct Abel inversion of the Cl images allowed determination of the speed resolution of the apparatus, which was found to be $\sim 6\%$.²¹ The Abel-inverted image yielded a translational anisotropy parameter, β_0 , close to -1.0 for the photodissociation process, suggesting that collisional scrambling of the Cl velocity distribution prior to reaction is unlikely to be a serious problem in the present experiments.²¹

Acquisition of ion images of reactively scattered HCl was complicated by the presence of a cold background HCl signal arising from unwanted side reactions in the gas lines. This background signal was observed as a bright spot in the center of the HCl images, which could be minimized by using fresh gas mixtures every ≈ 3 h. Probe-only images of the background HCl were obtained after collection of each signal image and were subtracted from the signal images. However, since the background subtraction is imperfect (see Fig. 1), this central portion of the image was not used in the data analysis. It should be stressed that the region of the image obscured by the cold background signal corresponds to backward scattering of the HCl products with about half of the energy appearing as c.m. kinetic energy, and we do not believe this missing region of data significantly impairs the analysis.

B. Data analysis

The analysis method followed that developed to fit the Doppler-resolved laser induced fluorescence (LIF) profiles of the products generated in photon-initiated reactions.^{33,40-44} This procedure allows for the distribution of product c.m. velocities that arises from population of different internal quantum states in the butyl coproduct. The method relies on fitting Legendre moments of the image with a set of suitably chosen basis functions, and has been described in detail previously.²¹ We have also recently demonstrated the general approach by applying a similar analysis to photofragment ion images.⁴⁵



FIG. 1. (a) Background subtracted images and (b) Legendre moments of order 0 (----), 2 (----), and 4 (...) for HCl [v'=0, j'=1 (top), 3 (middle), and 6 (bottom)]. The error limits on the experimental Legendre moments of the images lie in the range 6%–14% for j'=0 to j'=6, as discussed in the Sec. II B.

tional kinetic energy release f_t can be written as a Legendre polynomial expansion

$$P(\theta, w) \equiv P(\theta, f_t) \left| \frac{df_t}{dw} \right|$$
$$= \frac{1}{4} \sum_{n,m} a_{nm} P_n(\cos \theta) P_m(f_t') \left| \frac{df_t'}{dw} \right|, \qquad (3)$$

where *w* is the c.m. speed of the HCl,

$$f'_t = (2f_t - 1)$$

and

$$\left. \frac{df'_t}{dw} \right| = 2M \frac{m_{\rm HCl}}{m_{\rm C_4H_{10}}} \frac{w}{E'_{t,\rm max}}$$

The maximum possible kinetic energy release $E'_{t,\max}$ is given by

$$E'_{t,\max} = -\Delta_r H_0^{\theta} + E_t + E_{C_4 H_{10}} - E_{HCl}$$

In these equations *M* is the total mass, E_t is the collision energy, and $E_{C_4H_{10}}$ and E_{HCl} , appearing in the final expression, are the average internal energy of the C₄H₁₀ precursor (taken to be zero) and the *fixed* internal energy of the probed HCl quantum state, respectively. The moments of the c.m. distribution were assumed to be independent of the comparatively narrow spread of reactant relative speeds, v_r . For a reaction initiated by linearly polarized photolysis radiation, the corresponding lab frame velocity distribution takes a particularly simple form. We define the lab frame with the *z* axis parallel to the photolysis polarization vector ϵ , and the *x* axis along the photolysis propagation vector. (Note that for the pump-probe geometry employed in this work, the photolysis propagation and electric vectors lie in the image plane, i.e., the *xz* plane.) In the absence of rotational alignment effects, which tend to be small for HCl due to efficient hyperfine depolarization,^{46,47} it has been shown^{33,43,48,49} that integration of the joint c.m. scattering distribution of Eq. (3) over the reagent and precursor velocities leads to the lab velocity distribution

$$P(v,\Theta_v) = \sum_L B_L(v) P_L(\cos\Theta_v)$$
(4)

with L=0 and 2, and where Θ_v is the angle between the photolysis ϵ vector and the HCl lab velocity vector **v**. $P_L(...)$ are the Legendre polynomials. Explicit expressions for the $B_L(v)$, which are proportional to the bipolar moments $\overline{b}_0^L(L0;v)$ averaged over all reagent velocities, have been presented previously in the context of Doppler profile analysis.^{33,43} $B_0(v) \equiv P(v)$ is the lab speed distribution of the products, and the lab frame translational anisotropy is $\beta(v) = B_2(v)/B_0(v)$.

The expression for a simulated ion image $I(v_p, \phi)$ may be obtained by integrating Eq. (4) over v_y . This yields

$$I(v_p, \phi) = \sum_L M_L(v_p) P_L(\cos \phi), \qquad (5)$$

where v_p and ϕ are the radial and angular polar coordinates of the image, and the nonzero moments $M_L(v_p)$ are given by

$$M_{0}(v_{p}) = \int_{0}^{\infty} \left[2B_{0}(v) + \left(\frac{v_{p}^{2}}{v^{2}} - 1 \right) B_{2}(v) \right] \\ \times \left(\frac{v^{2}}{v^{2} - v_{p}^{2}} \right)^{1/2} dv$$
(6)

and

$$M_{2}(v_{p}) = \int_{0}^{\infty} \left(\frac{v_{p}^{2}}{v^{2}}\right) 2B_{2}(v) \left(\frac{v^{2}}{v^{2} - v_{p}^{2}}\right)^{1/2} dv.$$
(7)

The present analysis relies on using Eqs. (6) and (7) to generate sets of basis functions, $b_L(n,m;v_p)$ which are then fitted to the experimental data. The basis functions were obtained by replacing the full c.m. frame joint distribution of Eq. (3), used to simulate $M_L(v_p)$, by the product of two Legendre polynomials, $P_n(\cos \theta)P_m(f'_t)$. The basis functions were generated by Monte Carlo integration of the relevant terms in the c.m. scattering distribution over all reactant and precursor velocities, in much the same way as previously performed for Doppler-profile analysis.⁴⁴ A translational beam temperature transverse to the beam direction of 50 K was assumed, which (as noted in Sec. II A) provides a good description of the images obtained for background HCl. The

basis functions also allowed for the instrument resolution, which was estimated from Cl-atom photofragment images (see Sec. II A).

Low order experimental image moments $\mathcal{M}_L(v_p)$ were obtained by integration of the image over angular coordinate ϕ :

$$\mathcal{M}_{L}(v_{p}) = \frac{1}{2} \int_{-1}^{1} \mathcal{I}(v_{x}, v_{z})(2L+1)$$
$$\times P_{L}(\cos\phi)v_{p}d\cos\phi, \qquad (8)$$

where $\mathcal{I}(v_p, \phi) \equiv \mathcal{I}(v_x, v_z)v_p$, and v_x and v_z are the appropriate projections of the lab velocity in the image plane (proportional to the pixel coordinates of the image). Recall that in the present experiments the only nonzero moments of the image are those with L=0 and 2. The experimental image moments $\mathcal{M}_L(v_p)$ for L=0 and 2 were then fit *simultaneously* using the simulated moments $M_L(v_p)$ generated from a linear combination of the basis functions $b_L(...)$

$$M_L(v_p) = \sum_{nm} a_{nm} b_L(n,m;v_p).$$
(9)

The fitting coefficients a_{nm} were determined by minimizing χ^2 for the fit using a genetic algorithm subroutine, in which the fitting coefficients were constrained to lie within their physical limits. The choice of basis function ensures that the coefficients returned by the fit, a_{nm} , correspond to the moments of the joint c.m. distribution given in Eq. (3). Satisfactory fits to the data could be obtained by assuming a joint c.m. distribution of separable form, for which the a_{nm} coefficients may be set equal to $a_n \times d_m$, where a_n and d_m are the coefficients for the Legendre expansion of the angular and kinetic energy release distributions, respectively. Converged fits to the data were obtained with four moments in $\cos \theta$ and four moments in f_t (also see Sec. III).

The error limits on $P(\cos \theta)$ and $P(f_t)$ were determined using a Monte Carlo technique, described in detail elsewhere.⁵⁰ The error limits on the fitted experimental moments were determined to range from 6% to 14% of the zeroth order moment for j'=0 to j'=6, based on the variation in the moments obtained from individual ion images. These error limits were used to determine the threshold χ^2 values employed in the Monte Carlo error analysis (see Ref. 50 for details of this procedure).

III. RESULTS

A. Images and Legendre moments

Representative velocity-map ion images and the corresponding zeroth, second, and fourth order Legendre moments are shown in Fig. 1 for HCl (v'=0, j'=1, 3, and 6) (the images have been background subtracted and quadrant averaged for clarity). It can be seen, particularly in the zeroth order image moments, that the intensity shifts towards the center of the images with increasing HCl rotational state. This change in the intensity distribution could reflect either more backwards scattering or lower kinetic energy releases associated with the HCl products formed in higher rotational states. It should also be noted that, within the experimental



FIG. 2. Zeroth and second order Legendre moments (-----), and fits to those moments (-----), assuming H-atom abstraction from either only primary (left) or only secondary (right) carbon atoms. From top to bottom, data are shown for HCl (v'=0), products born in j'=0, 3, and 6. The fits were performed using basis function sets with four moments each in the c.m. angular scattering distribution and the kinetic energy release distribution.

signal-to-noise ratio of the data, the fourth order Legendre moments are very close to zero. This suggests that any angular momentum polarization of the HCl products has little influence on the form of the image moments, as consistent with the analysis described in Sec. II B.

Owing to the arrangement of the experimental apparatus used, it was not possible to scan the probe laser reliably over the extended wavelengths required to obtain the full rotational structure of the REMPI spectrum of the nascent HCI reaction products, and therefore the rotational population distribution was not determined. However, on the basis of the observed signal intensities for each transition studied, the rotational Boltzmann temperature was estimated qualitatively to be 180 ± 50 K. The rotational population distribution at this temperature peaks quite narrowly at j'=2, with a short tail extending to j'=9. These data are discussed further in Sec. IV.

B. Angular and kinetic energy release distributions

Initial fits to the data were attempted assuming the HCl product signal arose exclusively from H-atom abstraction at *either* primary *or* secondary carbon sites. The resulting fits to the data are shown in Fig. 2 for HCl products born in v' = 0, j' = 0, 3 and 6. In the case of abstraction occurring from primary carbon atoms only, the quality of the fits is seen to decrease drastically with increasing HCl rotational excitation. The high velocity sections of the experimental moments for the three rotational states are seen to be poorly reproduced by the fits. In addition, the fits to the second order Legendre moments, which are sensitive to the velocity-dependent translational anisotropy, show structure sharper than seen in the experimental data. The fits obtained using basis sets calculated by assuming that product formation oc-

curs exclusively through abstraction from secondary carbon atoms, although much better than those for abstraction from primary carbon atoms only, are seen to show the opposite trends, with the fits increasing in quality for products formed in higher rotational states, and the returned L=2 moment fits at low j' found to be broader than those determined experimentally. Qualitatively, these observations suggest that reaction at a primary carbon atom tends to produce HCl in low rotational states, while reaction at a secondary carbon atom favors production of higher rotational states of HCl (see below).

A more plausible analysis, which allows for both reaction pathways and the relative contribution of each to the total signal, yields the fits shown in Fig. 3. In this case, the c.m. angular scattering and fractional kinetic energy release distributions are constrained to be the same for reactions involving abstraction of either a primary or secondary H atom (as justified below). This approach allows the relative contribution of each reaction channel to be determined. Inclusion of both reaction pathways is found to improve the quality of the fits for the HCl(v'=0) products formed in low rotational states, as indicated by significant reductions in χ^2 compared with the values obtained assuming only primary or secondary H-atom abstraction (see Fig. 2). For the HCl (v'=0, j'=6) products, however, the value of χ^2 is unchanged by inclusion of the primary H atom abstraction channel, reflecting the fact that the vast majority of the HCl products in this rotational state are formed by abstraction from a secondary carbon atom (see below). The conclusions that both primary and secondary abstraction channels contribute to reaction is in accordance with the previous photon-initiated experiments using isotopically substituted alkanes by Varley and Dagdigian²⁴⁻²⁶ and Koplitz and co-workers.²³

Fits to the experimental Legendre moments were also carried out allowing different c.m. angular scattering and fractional kinetic energy release distributions to be associated with each channel (i.e., the channels were treated nonseparably). The χ^2 values returned from these fits were not found to be significantly lower than those obtained from the more constrained fits performed above, despite requiring almost double the number of fitting parameters. After appropriate averaging, the c.m. angular scattering and kinetic energy release distributions for each reaction pathway returned from these fits were seen to be in very good agreement with those obtained when the distributions are constrained to be the same for each reaction channel. The derived branching ratios also showed the same trends as those obtained from the more constrained analysis. For these reasons, it was felt that constraining the c.m. angular scattering and fractional kinetic energy release distributions to be the same for reactions involving abstraction of either a primary or secondary H atom was warranted.

The angular and energy resolutions of the current study were determined by investigating the dependence of the returned distributions and the primary-to-secondary abstraction channel weighting on the number of fitted moments employed, as shown in Fig. 4 for HCl (v'=0, j'=0, 3, and 6). The truncation point for the number of basis functions used was determined by observing the dependence of χ^2 on the



FIG. 3. Zeroth and second order Legendre moments (----), and fits to those moments (----) for HCl (v'=0, j'=0) (top) through to HCl (v'=0, j'=6) (bottom). The fits were performed using basis function sets with four moments each in the c.m. angular scattering distribution and the kinetic energy release distribution. The very low speed section of the moments ($v_p < 255 \text{ ms}^{-1}$) was not included in the fits, as discussed in Sec. II B. The error limits on the experimental Legendre moments of the images lie in the range 6%–14% for j'=0 to j'=6 as discussed in the Sec. II B.

number of fitting coefficients employed. In the present case, χ^2 did not decrease by a significant amount with inclusion of more than four moments in either the c.m. angular scattering distribution or the kinetic energy release distribution, indicating that the experiment is insensitive to features of the scat-



FIG. 4. The dependence of the returned c.m. angular scattering (left) and kinetic energy release (right) distributions on the number of moments employed. From the top, the data are for HCl (v'=0, j'=0, 3, and 6). The solid lines represent fits to the data using four moments in the CM angular scattering distribution and four moments in the kinetic energy release distribution. The three dotted lines are fits with basis sets of dimension (n,m) = (3,3), (4,5), and (5,5). The relative weighting between the two reaction channels for each rotational state are within the error limits shown in Fig. 6 (see Table I).

tering distribution finer than can be described by a four-term Legendre expansion. The returned distributions and the relative weighting between the two reaction pathways are, however, remarkably consistent as the number of moments used is varied. The relative contributions of the two reaction channels associated with the distributions shown in Fig. 4 are given in Table I, and are all seen to lie with the 2σ error bounds of the final analysis.

The c.m. angular scattering and kinetic energy release distributions for HCl (v'=0, j'=0-6) returned from the fits are shown in Fig. 5. A steady trend is seen in the c.m. angular scattering distributions, with the predominantly forward scattering of HCl products formed in low rotational states shifting to more isotropic scattering for the HCl products formed in the highest rotational states. The kinetic energy release distributions are insensitive to HCl rotational state, with only a modest trend towards higher kinetic energy release with higher HCl rotational excitation. Note that the f_t values shown on the x axes in Fig. 5 refer to the fractional energy release for the specific HCl quantum state in question.

The relative contributions from pathways (1) and (2) are plotted against rotational state in Fig. 6. In general, primary H-atom abstraction is seen to be largely associated with low rotational excitation of the HCl (v'=0) products, while abstraction of a secondary H atom dominates for HCl (v'=0) products produced with higher rotational energies; this is in good agreement with the qualitative conclusion drawn from the single channel fits. The nascent HCl product rotational population distributions for the two pathways may be calculated using the Boltzmann rotational temperature of 180

TABLE I. Relative contributions of the reaction pathways involving abstraction of a H atom from primary (1°) and secondary (2°) carbons sites determined from fits using basis sets generated with *n* Legendre moments in the c.m. angular scattering distribution and *m* Legendre moments in the kinetic energy release distribution. The c.m. distributions returned from these fits are shown in Fig. 4. Error limits for the optimum (4,4) fit represent 2σ errors resulting from statistical errors in the fit; these data are shown in Fig. 6.

$\operatorname{HCl}\left(v'=0,j'\right)$										
	0		3		6					
(n,m)	1°	2°	1°	2°	1°	2°				
(3,3)	0.70	0.30	0.42	0.58	0.00	1.00				
(4,5)	0.61	0.39	0.44	0.56	0.03	0.97				
(5,5)	0.61	0.39	0.43	0.57	0.03	0.97				
(4,4)	0.73 (±0.16)	0.27 (±0.16)	0.47 (±0.15)	0.53 (±0.15)	0.00 (±0.23)	1.00 (±0.23)				

K estimated in the preceding section for the total HCl(v' = 0) signal, in conjunction with the relative contributions of each reaction pathway (see Fig. 7). The rotational population distributions obtained in this way show the HCl products of



FIG. 5. Returned c.m. angular scattering (left) and kinetic energy release (right) distributions for HCl (v'=0, j'=0) (top) through to HCl (v'=0, j'=6) (bottom). Optimum fits to the data were obtained with four moments in both the c.m. angular scattering distribution and the kinetic energy release distribution. Error bars represent 2σ errors resulting from statistical errors in the fits, which include estimates of the error limits on the experimental image moments, as discussed in Sec. II B. Note that in the right-hand panels, the f_t scale refers to the state-specific fractional kinetic energy release, which does not include the rotational energy in the HCl product (see Table II).

secondary H-atom abstraction to be significantly rotationally hotter than those of primary H-atom abstraction. The overall branching ratios determined from these population distributions show that $52\% \pm 6\%$ of products are formed by abstraction of hydrogen from primary carbon atoms, while $48\% \pm 6\%$ are the products of secondary H-atom abstraction. Allowing for the 3:2 statistical abundance of primary to secondary H atoms, this corresponds to abstraction of an atom in the secondary position being favored by a factor of 1.4 ± 0.4 over that of abstraction of an atom in the primary position. It should be borne in mind that the value determined for this ratio is sensitive to the estimate made of the HCl rotational temperature, and is thus subject to relatively large errors.

The mean values obtained from the fractional kinetic energy release distributions shown in Fig. 5, $\langle f_t \rangle$, corrected for the HCl (v' = 0, j') rotational energy, are given in Table II. The mean internal energies in the butyl fragments are seen to remain fairly constant with HCl rotational state for both reaction pathways. A weighted average over the HCl rotational quantum states investigated for each reaction channel gives the overall fraction of available energy deposited into the internal degrees of freedom of the *n*- and *s*-butyl radicals,



FIG. 6. The relative contributions to the HCl (v'=0,j') products by abstraction of H-atoms from primary carbon atoms $(--\blacksquare--)$ and secondary carbon atoms $(--\bigcirc--)$. Error bars represent 2σ errors resulting from statistical errors in the fits, which include estimates of the error limits on the experimental image moments, as discussed in Sec. II B.

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FIG. 7. The rotational population distributions for the HCl (v' = 0, j') products formed by abstraction of H atoms from primary carbon atoms (-- \square --) and secondary carbon atoms (-- \square --), calculated using the relative contributions of each channel determined from the fits (see Fig. 6) and assuming a Boltzmann distribution for the total rotational population characterized by a rotational temperature of 180 K (-- \blacklozenge --). Error bars represent 2σ errors resulting from errors in the fits, which include estimates of the error limits on the experimental image moments, as discussed in Sec. II B.

 $\langle f_{\text{int}}(n-C_4H_9)\rangle$ and $\langle f_{\text{int}}(s-C_4H_9)\rangle$, as ~0.3 in both cases. The weights for each quantum state for each channel used in calculating this average were taken from the HCl(v' = 0, j') rotational populations shown in Fig. 7.

The data shown in Figs. 5 and 7 may be used to create two-dimensional (2D) contour maps and the corresponding 3D "wireframe" plots of the product flux as a function of HCl speed and c.m. scattering angle $P(w, \theta_t)$. Plots are shown for the products of H-atom abstraction from primary only, secondary only, and both carbon sites in Fig. 8. In generating these plots, the c.m. angular scattering and kinetic energy release distributions for the individual HCl rotational states have been averaged using the same weighting factors as above. The contour map for primary H-atom abstraction is seen to have a smaller radius than that for secondary H-atom abstraction, reflecting the lower exothermicity of this reac-



FIG. 8. Contour map and wireframe plots of the product velocity-angle flux averaged over HCl rotational state for abstraction of H atoms from (a) primary and (b) secondary carbon sites. Plots (c) correspond to the total flux for the reaction, where both primary and secondary H atoms are abstracted. The plots were obtained using the results shown in Figs. 5 and 7.

180°

tion pathway. The broader angular scattering distribution seen for secondary H-atom abstraction results from the greater contribution to rotationally excited HCl(v'=0)products by this reaction pathway. The contour map calculated for the overall reaction including both pathways mimics the results that would be obtained from a crossed molecu-

TABLE II. HCl (v' = 0, j') state-resolved, and state-averaged energy disposal data for the two pathways in the Cl plus *n*-butane reaction. The data have been obtained assuming mean available energies of 3280 cm⁻¹ for primary H-atom abstraction and 4510 cm⁻¹ for secondary H-atom abstraction. The errors on the state-resolved $\langle f_t \rangle$ values are typically ± 0.05 . The averaging over rotational state was performed using a Boltzmann rotational population distribution calculated at 180 K for the HCl (v' = 0) products, weighted by the contribution of each pathway for the rotational state in question. HCl (v' = 1) has been shown to be produced in negligible quantities in the reactions of Cl with both propane and *i*-butane at similar collision energies,^{25,26} and is thus neglected, despite being energetically accessible in both reaction pathways.

	Cl+n-	$Cl+n$ -butane \rightarrow HCl+ n - C_4H_9			$Cl+n$ -butane \rightarrow HCl+s-C ₄ H ₉		
HCl(v'=0,j')	$f_{\rm rot}({\rm HCl})$	$\langle f_t \rangle$	$\langle f_{\rm int}(n-{\rm C}_4{\rm H}_9)\rangle$	$f_{\rm rot}({\rm HCl})$	$\langle f_t \rangle$	$\langle f_{\rm int}(s-{ m C}_4{ m H}_9) \rangle$	
0	0.00	0.72	0.28	0.00	0.73	0.27	
1	0.01	0.75	0.24	0.00	0.76	0.24	
2	0.02	0.67	0.31	0.01	0.68	0.31	
3	0.04	0.62	0.34	0.03	0.64	0.33	
4	0.06	0.66	0.28	0.05	0.68	0.28	
5	0.10	0.68	0.23	0.07	0.70	0.22	
6	0.14	0.59	0.27	0.10	0.62	0.28	
Average	0.02	0.69	0.29	0.04	0.68	0.28	

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180°

lar beam experiment without product quantum state resolution.

IV. DISCUSSION

A. Rotational population distribution

The HCl rotational temperature estimated here (180 ± 50) K) is in reasonable agreement with that obtained for the Cl plus propane reaction by Varley and Dagdigian,²⁵ but is slightly hotter than that estimated for the Cl+CH₃CD₂CH₃ reaction (70-100 K) studied by Koplitz and coworkers,²³ and that determined for the Cl plus *i*-butane reaction (120 K) by Varley and Dagdigian.²⁶ The differences are thought to reflect (a) the number of primary and secondary or tertiary H-atoms available in the alkane reactants (there are six primary and four secondary H atoms in n-butane, while there are nine primary H atoms and only one tertiary H atom in *i*-butane), and (b) the higher exothermicity associated with abstraction of H-atoms from secondary and tertiary carbon sites compared with primary carbon sites. It is noteworthy that the product HCl rotational population distribution estimated here for the HCl products of the reaction of chlorine atoms with *n*-butane is very similar to that determined by Varley and Dagdigian for the reaction of atomic chlorine with propane.²⁵ This similarity reflects the comparable ratios of primary to secondary H-atoms in propane and n-butane, and the similar exothermicities of the respective channels in the two reactions.

According to the distributions shown in Fig. 7, the HCl products of primary H-atom abstraction are formed with an average rotational energy of around 60 cm^{-1} , while secondary hydrogen abstraction yields an average HCl rotational energy of $\sim 170 \text{ cm}^{-1}$. This degree of rotational excitation in the products of the two reaction pathways is again in reasonable agreement with the results of Varley and Dagdigian for the $Cl+CD_3CH_2CD_3$ and $Cl+(CH_3)_3CD$ reactions, where in the former the average rotational energies were found to be 84 and 110 cm⁻¹ for the DCl and HCl products, respectively,²⁵ while in the latter the HCl and DCl products were found to have average rotational energies of 50 and 100 cm⁻¹, respectively.²⁶ Each of these studies suggest that the HCl products of the reaction at a primary site are born colder than those from secondary attack, in qualitative agreement with the present findings.

B. Branching fraction

The relative reactivity of the primary and secondary carbon sites is in broad agreement with that obtained from the kinetics experiments performed by Tyndall *et al.*¹⁴ and Sarzynski and Sztuba.¹⁷ The kinetic studies show a more pronounced reactivity of the secondary site than observed here, possibly reflecting the different collision energy distributions in the thermal measurements, together with the different activation energies for the two reaction pathways. The positive activation energy for abstraction of hydrogen from primary carbon sites indicates a barrier in this reaction pathway, while no such barrier is present for secondary H-atom abstraction, where the activation energy is found to be negative.¹⁷ The thermalized Cl atoms used in the kinetic studies provide a mean collision energy of only ~ 0.04 eV, with the result that the barrierless abstraction of H atoms from secondary carbon sites is favored over abstraction of H atoms from primary carbon sites. The much higher collision energies of around 0.32 eV afforded by Cl₂ photolysis, however, are sufficient to surmount the barrier to primary H-atom abstraction, resulting in more equal reactivities of the two carbon atom sites observed in the current study.

The reactivity enhancement for secondary H-atom abstraction obtained here is also somewhat lower than observed in the photoloc studies of the Cl plus propane reaction.^{23,25,26} Koplitz and co-workers found abstraction of hydrogen or deuterium atoms from the secondary carbon site to be favored by a factor of 2-3 over abstraction from a primary carbon site in the Cl+CH₃CD₂CH₃ and Cl+CD₃CH₂CD₃ reactions,²³ while Varley and Dagdigian found abstraction from the secondary carbon site to be favored by a factor of 2.7 ± 0.5 over that from the primary site in the Cl $+ CD_3 CH_2 CD_3$ reaction.²⁵ The latter authors also found abstraction of the deuterium atom from the tertiary carbon site in $(CH_3)_3CD$ to be a factor of 2.7±0.3 more reactive than the primary carbon sites.²⁶ The comparison between the present work and the previous photoloc studies is complicated by kinetic isotope factors, which will also affect the H/D-atom abstraction reactivity, together with differences in collision energy distribution. The study of the Cl $+CD_3CH_2CD_3$ reaction by Varley and Dagdigian²⁵ is probably the most directly comparable with the present work (both in terms of system and the collision energy conditions employed). The difference in enhancement obtained by Varley and Dagdigian,²⁵ compared with that found here, could well be due to isotope effects, which will raise the effective barrier for abstraction of a deuterium atom from a (primary) C-D bond over that of an H atom from a (secondary) C-H bond.

C. Angular scattering distributions

The c.m. angular scattering distributions shown in Fig. 5 are in good agreement with those recently obtained by Toomes and Kitsopoulos from images recorded using the unskimmed crossed molecular beam technique.²⁹ Note also that they are very similar to those obtained previously for the Cl plus ethane reaction.^{21,29} Comparison of the total c.m. velocity-angle flux map generated for the Cl plus n-butane reaction shown in Fig. 8 with that obtained by Suits and co-workers for the Cl plus propane reaction²⁷ reveals that more forward scattering is seen in the current photoloc study than in the crossed molecular beam experiment. Also contrary to that work, here we find that abstraction of an H atom from a primary carbon site is associated predominantly with forward scattering, while more isotropic and less forward peaked scattering is seen for the products of secondary H-atom abstraction (see further discussion in Sec. IV D).

The differing propensities in the c.m. angular scattering of the products formed in the two abstraction pathways, and the different HCl product rotational excitation associated with each, suggests that somewhat different mechanisms are needed to explain the dynamics of the Cl plus *n*-butane system. Consider first the mildly exothermic primary H-atom abstraction channel, producing forward scattered products and HCl formed in low rotational states. The dynamical characteristics of this abstraction pathway closely match those of a peripheral chemical reaction, in which forward scattering from a direct exoergic atom transfer reaction is proposed to be an indication of abstraction of an atom at the periphery of a reagent.⁵¹ As was mentioned in Sec. I, transition state calculations on the Cl plus propane and Br plus *n*-butane systems suggest that the optimum geometry for both abstraction channels in the Cl plus *n*-butane reaction is likely to be that in which the Cl-H-C atoms are arranged collinearly. In this arrangement, the impact parameter b for the abstraction of an H atom from a primary carbon site is necessarily nonzero and relatively large. This corresponds to an opacity function P(b) for this reaction pathway which is zero (or very small) at low b and peaks at impact parameters on the order of the distance from the center of mass of the *n*-butane molecule to the chlorine atom in the transition state, ~ 4 Å (i.e., the periphery of the *n*-butane molecule).

The more exothermic abstraction of an H atom from a secondary carbon site produces a broader, forward peaking, scattering distribution, with greater HCl rotational excitation. As for abstraction of an H atom from a primary carbon site, this reaction pathway is expected to be direct and to have a collinear transition state. From similar considerations to those used in the primary reaction channel, the estimated range of impact parameters over which the opacity function for this reaction pathway is nonzero extends from b=0 to ≈ 2.5 Å. For a direct reaction occurring primarily at low impact parameters, products are expected to be predominantly backward scattered. While the observed scattering is not as extreme as this, greater backwards and sideways scattering is seen for this reaction pathway than for abstraction of an H atom from a primary carbon site, and a more reboundtype mechanism is thus suggested for this reaction channel. This is consistent with the higher rotational excitation found for the HCl products formed in this reaction pathway. Forward scattering of the products of collisions taking place at lower impact parameters may be taken to be an indication of a wide cone of acceptance, where the approach of the chlorine atom is not tightly constrained to be collinear with the breaking C-H bond. Release of energy along the axis of the C-H bond for these slightly bent transition states yields rotational excitation of the HCl products, as observed for this reaction pathway. The observed scattering dynamics can thus be qualitatively accounted for through this interplay between the impact parameter and the angle of approach of the reactants.

D. Energy partitioning

On average, just under 30% of the available energy is seen to be channeled into the internal modes of both the *n*and *s*-butyl radical coproducts. Owing to the different exothermicities for the two reaction pathways, this corresponds to energies of around 950 and 1260 cm⁻¹ being partitioned into internal excitation of the *n*-butyl and *s*-butyl cofragments, respectively. The HCl rotational state resolved product speed distributions obtained from the unskimmed crossed beam experiments by Toomes and Kitsopoulos suggest a similar level of excitation of the internal modes in the butyl coproducts, despite differentiation between the two reaction pathways not being possible in their study.²⁹ The mean fractions of the total available energy found in internal excitation of the *n*-butyl and *s*-butyl cofragments in the present investigation are slightly higher than the 22% found for the ethyl radical products of the Cl plus ethane reaction,²¹ probably reflecting the higher collision energy employed in the Cl plus *n*-butane reaction, and the greater number of low energy internal modes in the butyl radical compared with the ethyl radical. The level of rotational excitation of the HCl products is very similar in the two reaction systems.

In their crossed molecular beam study on the reaction of chlorine with propane, Suits and co-workers found 40%-50% of the available energy was deposited into the internal modes of the HCl and propyl products, and concluded that most of this energy resides in the propyl radicals.²⁷ This is a significantly greater internal excitation of the alkyl cofragment than found here for the Cl plus n-butane reaction, or previously for the Cl plus ethane reaction.²¹ Also note that more backward scattering was seen in the Cl plus propane crossed molecular beam study than in our photoloc investigations of Cl plus butane and ethane.²¹ These two observations are likely to be linked, and may be symptomatic of a systematic error, either in the photoloc experiments, or in the crossed molecular beam experiments of Suits and co-workers.^{27,28} In the latter case, the alkyl fragments were detected using vacuum ultraviolet synchrotron radiation (with a photon energy of 9.5 eV) to effect photoionization of the alkyl radicals, with the resulting ions detected mass spectrometrically. If alkyl radical products born with excited internal modes were preferentially ionized in that study, then the data obtained would be biased towards greater internal excitation of the alkyl products. Furthermore, Suits and coworkers have subsequently suggested that photoionization of alkyl radicals at 7.9 eV is relatively insensitive to primary alkyl radical products.⁵² If photoionization at 9.5 eV also showed a similar, though presumably more modest, bias against detection of (forward scattered) primary products, this would explain why the molecular beam experiments display more backward scattering, and more internal excitation, than the present study. A similar difference between the results of crossed molecular beam experiments using photoionization of alkyl products by Suits and co-workers and those from photoloc studies of the cofragments has been seen in the reactions of $O({}^{3}P)$ with saturated hydrocarbons.^{53–55} Bulb experiments carried out by Kajimoto and co-workers with Doppler-resolved LIF detection of the OH fragments find the products of the reactions of $O({}^{3}P)$ with *i*-butane and cyclohexane to be almost isotropically scattered.^{56,57} In the case of the $O({}^{3}P)$ plus *c*-hexane reaction, around 60% of the available energy was seen to be deposited into the cyclohexyl products. At similar collision energies, however, Suits and co-workers found the *i*-butyl and *c*-hexyl fragments to be strongly backward scattered, with a slightly greater fraction of the available energy found as internal excitation of the alkyl products.54

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The internal excitation of the *n*-butyl and *s*-butyl radical products may reside in rotational and/or vibrational degrees of freedom. Consider first the abstraction of an H atom from a primary carbon site in *n*-butane. Assuming the product *n*-butyl radical is well approximated as a near-prolate symmetric top with a rigid carbon frame, its rotational levels are given approximately by

$$F(J,K) \simeq \overline{B}J(J+1) + (A-\overline{B})K^2, \qquad (10)$$

where, assuming the *n*-butyl radical adopts the lowest energy conformation, the average rotational constant about the b or c axes, $\overline{B} = 0.5(B+C)$, is calculated to be ~0.123 cm⁻¹, with $A \simeq 0.827 \,\mathrm{cm}^{-1}$. If all the energy observed to be channeled into internal excitation of the *n*-butyl radicals was rotational in origin, in the two extreme cases this would correspond to end-over-end rotational excitation of n-butyl to J \approx 88, K=0, or rotational excitation about the *a* axis to J $=K \approx 34$. Similar considerations to those used in the discussion of the internal excitation of the ethyl product of the Cl plus ethane reaction,²¹ where an impulsive release of the reaction exothermicity along the breaking C-H bond in the transition state geometry was assumed to impart a torque on the ethyl fragment, leads to the prediction of n-butyl rotational angular momenta of $\sim 40\hbar$ for end-over-end rotation, or of $\sim 25\hbar$ about the *a* axis. This estimate is a lower limit, since the energy found to be partitioned into the *n*-butyl radical is greater than the reaction exothermicity. In a peripheral mechanism, higher torques may be expected to be imparted on the *n*-butyl radical from abstraction of the H atom by a fast moving chlorine atom. Note that the actual rotation is likely to be about all three axes with intermediate values of J and K, since the breaking C-H bond is not necessarily in the plane of the carbon backbone. End-over-end rotation is expected to dominate, however, due to the larger torque exerted for this motion.

For the secondary H-atom abstraction channel, the rotational constants for the s-butyl radical product can be estimated to be $\bar{B} = 0.5(B+C) \simeq 0.118 \text{ cm}^{-1}$, and $\simeq 0.891 \,\mathrm{cm}^{-1}$. The maximum rotational state accessible if all the observed available energy deposited into internal modes of the s-butyl is found as end-over-end rotation is J \simeq 104, K = 0, while for rotational excitation about the *a* axis, $J = K \approx 38$. Impulsive release of the reaction exothermicity along the breaking C-H bond in the transition state is not expected to yield such high levels of end-over-end rotation, but is more likely to excite rotation about the *a* axis. The axis of the breaking bond passes very close to the c.m. of the s-butyl, thus an impulse will exert only a very small torque on the newly forming radical, and, owing to the high moments of inertia about the b and c axes, will yield only modest levels of end-over-end rotational excitation. Using a transition state geometry based on the structure of *n*-butane, this is indeed seen to be the case, with end-over-end rotational angular momenta of only $\sim 34\hbar$ found to be generated. The moment of inertia about the *a* axis is much lower, however, and the component of the impulse about this axis is thus expected to induce higher levels of excitation about this axis. Rotational angular momenta of $\sim 28\hbar$ are calculated to be generated for rotation about the *a* axis. The main rotational excitation of the *s*-butyl products is thus likely to be around the *a* axis. As in the case of the *n*-butyl radical, in practice rotation will be about all three axes, with lower values for *J* and *K* than predicted from the extremes presented here.

Energy release into the vibrational modes of the butyl radical products may be associated with relaxation of the CH_2 or >C-H moieties from the pyramidal geometries expected to be adopted in the transition state, to the near planar arrangement in the products. This change in geometry could give rise to excitation of the out-of-plane CH₂ or >C-H rocking modes; the frequency of the out-of-plane CH₂ mode in *n*-butyl has been measured to be 520 cm^{-1} , and its motion is thought to be almost independent of the nonradical portion of the hydrocarbon chain.^{58–61} For the Cl plus ethane reaction it has been shown that a Franck-Condon model of the vibrational excitation of the CH2 rocking mode predicts unrealistic levels of vibrational excitation.²¹ From the similarities in the vibrational frequencies of the radical rocking modes and the associated transition state geometries, one would expect similar (i.e., unrealistic) levels of excitation to be predicted in the Cl plus n-butane reaction. However, lower levels of excitation could be generated if there was a more gradual relaxation of the geometry of the CH₂ moiety from the transition state to the products.

V. CONCLUSIONS

Rotational state resolved c.m. angular scattering and kinetic energy release distributions have been determined from experimental velocity-map ion images of the HCl (v'=0, j=0-6) products of the reaction of chlorine with *n*-butane. Analysis of the images suggests that abstraction of both primary and secondary H atoms occurs, and has allowed estimates to be made of the relative contributions of these two abstraction pathways for each HCl(v'=0) rotational quantum state investigated. Abstraction of an H atom from a primary carbon site is found to produce rotationally very cold HCl(v'=0) products which are forward scattered, whereas abstraction of an H atom from a secondary carbon site yields more isotropically scattered HCl products formed with higher rotational excitation. It is suggested that a peripheral reaction mechanism is responsible for the primary H atom abstraction channel, whilst a more rebound-type mechanism is seen to account for the dynamics of the secondary abstraction channel. The returned kinetic energy release distributions show that around 30% of the available energy is found as internal excitation of the *n*-butyl and *s*-butyl products. Possible sources of this excitation have been discussed.

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