Electronic Supplementary Information: Primary vs Secondary H-atom Abstraction in the Cl-Atom Reaction with *n*-Pentane

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S.1 Angular distributions measured at different probe beam heights

The velocity map images recorded in our dual molecular beam instrument show mostly forward scattered HCl products from Cl + *n*-pentane, with much weaker back scattering. However, Suits and co-workers previously reported a significant component of back scattered pentyl radical products from their crossed molecular beam experiments, although background signals interfered with the strong forward scattering peak.[1] The dual molecular beam technique uses a range of time delays between the photolysis and probe lasers to try to eliminate any bias in detection of products with faster or slower speeds, but products with low lab-frame speeds are more prone to secondary collisions with the beam of reactant molecules.[2] In contrast, crossed molecular beam measurements can suffer from bias towards detecting products with lower lab frame velocities.[3]

In the current study, further investigation of any detection bias was carried out for our dual molecular beam instrument by changing the probe laser beam height with respect to the alkane molecular beam. We reported previously that the detection probability of low-speed HCl products (i.e. those backward scattered in the centre of mass frame) decreases when the probe laser is aligned above the centre of an alkane molecular beam.[4] We therefore focused the probe laser beam 2-mm below the centre of the molecular beam to promote detection of back-scattered products and compared the images obtained to those with a probe laser beam focused 1-mm above the centre of the alkane beam. The angular scattering distributions from the two sets of measurements are shown in Fig. S1. In both cases, the products are measured to be strongly forward scattered, but the derived back-scattering propensity is slightly higher (at the expense of the forward scattered flux) when the probe laser beam is aligned below the alkane molecular beam. The results are also compared with the angular scattering distributions obtained by Suits and coworkers[1] for the Cl + *n*-pentane reaction at similar collision energies. For the images presented and analysed in the main paper, the probe laser was focused 0.5 – 1.0 mm above the centre of the *n*-pentane beam.

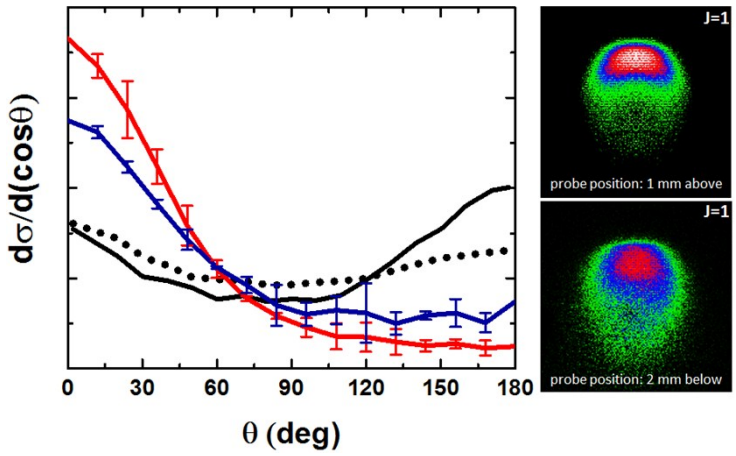

Fig. S1 Comparison of the angular distributions of HCl from the dual molecular beam experiment used in the current study, and of pentyl radicals from previous crossed molecular beam experiments (ref. 1) at a similar collision energy. The red and blue curves represent the angular distributions of HCl(v=0, J=1) from this work at probe positions of 1 mm above and 2 mm below the centre of the *n*-pentane molecular beam respectively. The corresponding velocity map images are shown on the right and were recorded at an average collision energy of 33.5 kJ mol^{-1}. The solid and dotted black curves are digitised from ref. 1 and show the angular distributions of pentyl radicals from the same reaction at collision energies of 21 kJ mol^{-1} and 35.3 kJ mol^{-1} respectively. All the distributions are normalized to sum to unity.

S.2 QCT simulation of geometric requirements for the Cl + *n*-pentane reaction

Calculation of the dependence of reaction probability on the initial orientation of the Cl atom with respect to the reactive C-H bond in *n*-pentane provides dynamical stereochemistry insights not available directly from the experimental measurements. In these calculations, the reference frame was defined with the ***z***-axis parallel to the reactive C-H bond axis. The polar and azimuthal angles (ψ,ϕ) illustrated in Fig. 10 define the asymptotic angle of approach of the Cl atom. The dependence of the reaction probability on this initial orientation was expanded in terms of real spherical harmonics, $Y_l^m(\psi,\phi)$:[5]

$$P(\psi,\phi) = \sum_{l=0}^{N_l} \sum_{m=0}^{l} a_{l,m} Y_l^m(\psi,\phi) \qquad (S1)$$

$$Y_l^m = \frac{i}{\sqrt{2}}\left[Y_{lm} - (-1)^m Y_{l-m} \right],\ m < 0$$

$$Y_l^m = \frac{1}{\sqrt{2}}\left[Y_{l-m} + (-1)^m Y_{lm} \right],\ m > 0$$

$$Y_l^0 = Y_{l0},\ m = 0$$

and $Y_{l,m}$ are the regular spherical harmonics. The expansion coefficients $a_{l,m}$ correspond to the expectation values of the basis functions as shown in Eq. (S2). The expansion was performed to numerical distributions deduced from a total of N_{sel} trajectories selected according to specific criteria, such as final state or reactive channel.

$$a_{l,m} = \langle Y_l^m(\psi,\phi) \rangle = \frac{1}{N_{sel}} \sum_i^{N_{sel}} Y_l^m(\psi_i, \phi_i) \qquad (S2)$$

S.3 Empirical valence bond force field

S.3.1 Atom types

The atoms of reactant and product molecules were assigned a type using the notation introduced in Table S1. The numbers in parentheses refer to the positions of the carbon atoms in pentane or the pentyl radical: C1 and C5 are primary C-atom sites; C2 and C4 are the two secondary carbon atoms attached to the primary ones; and the single C3 is the secondary carbon atom at the centre of the carbon atom backbone.

Table S1: Atom type assignments in pentane, pentyl radicals, and HCl

Type	Atom	Description
1	C	Csp^3 generic
11	C	Csp^3 CH_3 (C1,C5)
12	C	Csp^3 CH_2 (C2,C4)
13	C	Csp^3 CH_2 middle (C3)
2	C	Csp^2 generic
21	C	Csp^2 primary (C1)
22	C	Csp^2 second (C2,C4)
23	C	Csp^2 middle (C3)
5	H	H generic
30	Cl	Cl generic

S.3.2 Bond stretching energy terms

The energies associated with bond stretching between atoms of types *i* and *j* are described by a Morse potential:

$$E(r_{ij}) = D_{ij,0}\left[1 - \exp\left(-\beta_{ij}(r_{ij} - r_{ij,0})\right)\right]^2, \quad \text{(S3)}$$

where r_{ij} is the distance between the two atoms, $r_{ij,0}$ is their equilibrium distance, β_{ij} is the force constant, and $D_{ij,0}$ is the dissociation energy. The fitted parameters are listed in Table S2.

Table S2: Values of parameters in the Morse functions used to describe bond stretching potential energies between atoms of types i and j defined in Table S1.

i	*j*	b_{ij} / Å^{-1}	$r_{ij,0}$ / Å	$D_{ij,0}$ / (kJ mol^{-1})
1	1	1.40	1.53	511.69
1	2	1.79	1.49	668.82
1	5	1.70	1.10	549.02
2	5	1.65	1.09	511.09
5	11	1.86	1.10	493.94
5	12	1.86	1.10	493.94
5	13	1.86	1.10	493.94
5	21	1.65	1.09	511.09
5	22	1.65	1.09	511.09
5	23	1.65	1.10	511.09
11	12	1.40	1.53	568.88
11	22	1.79	1.50	668.82
12	13	1.40	1.53	568.88
12	21	1.79	1.50	668.82
12	23	1.79	1.50	668.82
13	22	1.79	1.50	668.82
5	30	1.80	1.28	505.98

S.3.3 Angle bending terms

Angle bending energy is described by a cubic polynomial function

$$E(\theta_{ijk}) = k_{2,ijk}(\theta_{ijk} - \theta_{ijk,0})^2\left[1 + k_{3,ijk}(\theta_{ijk} - \theta_{ijk,0})\right], \quad \text{(S4)}$$

where θ_{ijk}, is the angle between atom types *i*, *j* and *k*, $\theta_{ijk,0}$ is the equilibrium angle, and k_2 and k_3 are the quadratic and cubic force constants. The parameters are listed in Table S3 for atom types defined in Table S1.

Table S3: Values of parameters in the cubic polynomial function used to describe angle bending energy terms

.i	*j*	*k*	$\theta_{ikj,0}$ / °	$k_{2,ijk}$ / (kJ mol^{-1} °$^{-2}$)	$k_{3,ijk}$ / (kJ mol^{-1} °$^{-2}$)
1	1	1	112.60	0.14	-0.0009
1	1	2	113.40	0.12	-0.0010
1	1	5	110.00	0.06	-0.0008
1	2	1	120.20	0.09	-0.0009
1	2	5	119.20	0.04	0.0000
2	1	5	110.00	0.06	-0.0004
5	1	5	107.07	0.05	-0.0003
5	2	5	117.60	0.03	0.0003
5	11	5	107.82	0.05	-0.0003
5	11	12	111.20	0.06	-0.0008
5	12	5	106.50	0.05	-0.0003
5	12	11	109.60	0.06	-0.0008
5	12	13	109.10	0.06	-0.0008
5	12	23	109.42	0.06	-0.0004
5	12	21	109.92	0.06	-0.0004
5	13	5	106.30	0.05	-0.0003
5	13	12	109.26	0.06	-0.0008
5	11	22	111.40	0.06	-0.0004
5	13	22	109.60	0.06	-0.0004
5	21	5	117.76	0.03	0.0003
5	21	12	120.70	0.04	0.0000
5	22	11	118.74	0.04	0.0000
5	22	13	118.08	0.04	0.0000
5	23	12	118.25	0.04	0.0000
11	12	13	112.60	0.14	-0.0009
11	12	23	113.20	0.12	-0.0010
11	22	13	120.25	0.09	-0.0009
12	23	12	120.72	0.09	-0.0009

12	13	12	113.20	0.14	0.0000
12	13	22	113.74	0.12	0.0000
13	12	21	113.21	0.12	0.0000

S.3.4 Torsional terms

The torsional energy term for four linearly connected atoms is defined in Eqn. (S5).

$$E(\varphi_{ijkl}) = \sum_{a=1}^{3} \frac{1}{2} V_{a,ijkl}\left[1 - \cos\left(a\varphi_{ijkl} - \varphi_{ijkl,0}\right)\right] \quad \text{(S5)}$$

Here, φ_{ijkl} is the dihedral angle spanned by the atoms of types *i*-*j*-*k*-*l*, $\varphi_{ijkl,0}$ is the equilibrium dihedral angle, and $V_{a,ijkl}$ is the barrier height. No distinction was made between the various subtypes of C(sp^3) and C(sp^2) atoms. The fitted parameters are listed in Table S4.

Table S4: Values of parameters in the function used to describe torsional energy terms for atom types defined in Table S1.

i	*j*	*k*	*l*	$\varphi_{ijkl,0}$ / °	$V_{1,ijkl}$ / (kJ mol $^{-1}$ °$^{-2}$)	$V_{2,ijkl}$ / (kJ mol $^{-1}$ °$^{-2}$)	$V_{3,ijkl}$ / (kJ mol $^{-1}$ °$^{-3}$)
1	1	1	1	0.00	0.77	0.71	2.18
1	1	1	2	0.00	0.84	-0.84	5.44
1	1	1	5	0.00	0.00	0.00	1.32
1	1	2	1	0.00	0.42	0.84	3.35
1	1	2	5	0.00	0.00	0.00	0.04
1	2	1	5	0.00	0.00	0.00	2.26
2	1	1	5	0.00	0.00	0.00	2.09
5	1	1	5	0.00	0.00	0.00	1.58
5	1	2	5	0.00	0.00	0.00	0.04

S.3.5 Out-of-plane bending

The out-of-plane angle for the atom types *i*, *k*, *l*, connected to the centre, *j*, is defined as the angle between the *i*–*j* vector and the *i*–*k*–*l* plane. The functional form of the improper torsion energy term is the same as for the angle bending and is given by Eqn. (S4) apart from an extra quartic term. No distinction was made between the various subtypes of C(sp^3) and C(sp^2) atoms. The parameters are specified in Table S5.

Table S5: Values of parameters in the potential energy functions for out-of-plane bending

i	*j*	*k*	*l*	$\theta_{ikjl,0}$ / °	$k_{2,ijkl}$ / (kJ mol $^{-1}$ °$^{-2}$)	$k_{3,ijkl}$ / (kJ mol $^{-1}$ °$^{-3}$)	$k_{4,ijkl}$ / (kJ mol $^{-1}$ °$^{-4}$)
1	2	1	5	5.90	0.05	0.00092	0.00117
1	2	5	5	3.31	0.05	0.00092	0.00117
5	2	1	1	5.00	0.05	0.00000	0.00000
5	2	1	5	2.86	0.05	0.00000	0.00000

S.3.6 van der Waals interactions

The van der Waals interaction terms incorporated in the EVB force fields were modelled by the Buckingham–Corner four parameter function defined in Eqs. (S6)–(S7)

$$V(x_{ij}) = \varepsilon_{ij}\left(\frac{8-2c_{6,ij}}{\beta_{ij}-8}\exp\left[\beta_{ij}(1-x_{ij})\right] - c_{6,ij}x_{ij}^{-6} - c_{8,ij}x_{ij}^{-8}\right), \quad \text{(S6)}$$

$$x_{ij} = \frac{r_{ij}}{r_{ij,0}},$$

$$c_{8,ij} = \frac{6c_{6,ij} + \beta_{ij} - \beta_{ij}c_{6,ij}}{\beta_{ij}-8}.$$

In this function, r_{ij} is the distance between atoms *i*, *j*; $r_{ij,0}$ is the distance between these two atoms at the maximum well depth of ε_{ij}; β_{ij} is the repulsive force constant; and $c_{6,ij}$ and $c_{8,ij}$ are the coefficients of the attractive terms. To avoid the Buckingham catastrophe at short interatomic distances the attractive terms are multiplied by the exponential damping term of Eq. (S7) where $x_{ij} < 1$.

$$f(x_{ij}) = \exp\left[-4(x_{ij}-1)^3\right] \quad \text{(S7)}$$

No distinction was made between the various subtypes of C(sp^3) and C(sp^2) atoms. The optimised van der Waals parameters are listed in Table S6.

Table S6: Values of parameters in the Buckingham-Corner function for van der Waals interactions.

i	*J*	ε_{ij} / (kJ mol^{-1})	$r_{ij,0}$ / Å	β_{ij} / Å^{-1}	$c_{6,ij}$
1	5	0.65	3.20	9.61	3.54
2	5	0.65	3.20	9.61	3.54
1	30	2.09	3.78	11.09	3.22
2	30	2.09	3.78	11.09	3.22
5	5	0.10	2.51	14.09	3.59

5	30	0.19	4.00	12.00	3.55	

S.3.7 Reactive coupling terms

The coupling terms, V_{1N}, $1 \neq N$, between the reactant state and N-th product state were treated using two-dimensional Gaussian functions that depended on the reactive C—H and H—Cl distances. The exact form of the coupling term is given in Eqs. (S8) and (S9).

$$V_{1N} = A \exp\left[- b_{11}(r_{ij} - r_{ij,0})^2 + b_{22}(r_{jk} - r_{jk,0})^2 + b_{12}(r_{ij} - r_{ij,} \right. \quad \text{(S8)}$$

.

The coefficients in the exponent represent an equation of an ellipse to keep the matrix

$$\begin{bmatrix} b_{11} & \frac{b_{12}}{2} \\ \frac{b_{12}}{2} & b_{22} \end{bmatrix} = \begin{bmatrix} \frac{\cos^2\theta}{2\sigma_{ij}^2} + \frac{\sin^2\theta}{2\sigma_{jk}^2} & \frac{\sin 2\theta}{-4\sigma_{ij}^2} + \frac{\sin 2\theta}{4\sigma_{jk}^2} \\ \frac{\sin 2\theta}{-4\sigma_{ij}^2} + \frac{\sin 2\theta}{4\sigma_{jk}^2} & \frac{\sin^2\theta}{2\sigma_{ijC-H}^2} + \frac{\cos^2\theta}{2\sigma_{jk}^2} \end{bmatrix} \quad \text{(S9)}$$

positive semi-definite. Therefore, the coupling term cannot diverge for any *i*(C)—*j*(H) and *j*(H)—*k*(Cl) distances. In Eqn. (S8) and (S9), *A* is the amplitude of the coupling, $r_{ij,0}$ and $r_{jk,0}$ locate the centre of the Gaussian function, θ_{ijk} is the angle between the main axis of the Gaussian function and the C–H bond, and σ_{ij}^2 are the widths of the Gaussian function. Table S7 lists the fitted values of the parameters.

Table S7: Values of parameters used in the reactive coupling energy terms.

i(C)	*j(H)*	*k(Cl)*	*A* / (kJ mol^{-1})	$r_{ij,0}$ / Å	σ_{ij} / Å	$r_{jk,0}$ / Å	σ_{jk} / Å	θ_{ijk} / degrees
11	5	30	173.47	1.21	1.23	1.42	0.71	177.38
12	5	30	188.15	1.27	0.61	1.41	1.16	78.05
13	5	30	192.21	1.17	1.27	1.42	0.61	170.86

S.4 Geometries and frequencies of the stationary points from *ab initio* calculations

Reactants and products

pentane						
MP2	aug-cc-pVDZ					
Energy / (kJ mol^{-1})	Structure:	x / Å	y / Å	z / Å		Frequency / (cm^{-1})
0	C	2.4888	-0.3095	-0.0221	1	105
	H	2.5278	-1.0309	0.8107	2	111
	H	3.3874	0.3246	0.0377	3	175
	H	2.5393	-0.8799	-0.9642	4	246
	C	1.2047	0.5259	0.0408	5	254
	H	1.1866	1.1099	0.9785	6	393
	H	1.1977	1.2593	-0.7854	7	401
	C	-0.0602	-0.3354	-0.0401	8	728
	H	-0.0591	-1.0667	0.7894	9	759
	H	-0.0482	-0.9218	-0.9766	10	858
	C	-1.3528	0.4920	0.0218	11	877
	H	-1.3649	1.2234	-0.8063	12	939
	H	-1.3362	1.0974	0.9530	13	982
	C	-2.5941	-0.3472	-0.0211	14	1045
	H	-2.6003	-1.3428	0.4272	15	1075
	H	-3.5492	0.0728	-0.3391	16	1101
					17	1166
					18	1198
					19	1256
					20	1269
					21	1316
					22	1320
					23	1350
					24	1391
					25	1392
					26	1396
					27	1469
					28	1475
					29	1484
					30	1490
					31	1491
					32	1493
					33	1498
					34	3030
					35	3047

					36	3052
					37	3054
					38	3055
					39	3073
					40	3096
					41	3108
					42	3143
					43	3143
					44	3149
					45	3149
					ZPE	**422.28 kJ/mol**

pent-1-yl						
MP2	**aug-cc-pVDZ**					
Energy / (kJ mol^{-1})	**Structure:**	**x / Å**	**y / Å**	**z / Å**		**Frequency / (cm^{-1})**
14.50	C	2.4888	-0.3095	-0.0221	1	98
	H	2.5278	-1.0309	0.8107	2	113
	H	3.3874	0.3246	0.0377	3	132
	H	2.5393	-0.8799	-0.9642	4	179
	C	1.2047	0.5259	0.0408	5	251
	H	1.1866	1.1099	0.9785	6	390
	H	1.1977	1.2593	-0.7854	7	405
	C	-0.0602	-0.3354	-0.0401	8	471
	H	-0.0591	-1.0667	0.7894	9	723
	H	-0.0482	-0.9218	-0.9766	10	767
	C	-1.3528	0.4920	0.0218	11	865
	H	-1.3649	1.2234	-0.8063	12	910
	H	-1.3362	1.0974	0.9530	13	949
	C	-2.5941	-0.3472	-0.0211	14	1036
	H	-2.6003	-1.3428	0.4272	15	1081
	H	-3.5492	0.0728	-0.3391	16	1100
					17	1112
					18	1170
					19	1224
					20	1265
					21	1297
					22	1319
					23	1349
					24	1390
					25	1395
					26	1455
					27	1473

					28	1481
					29	1483
					30	1490
					31	1496
					32	2990
					33	3040
					34	3051
					35	3055
					36	3074
					37	3088
					38	3109
					39	3144
					40	3150
					41	3191
					42	3307
					ZPE	383 **kJ/mol**

pent-2-yl						
MP2	**aug-cc-pVDZ**					
Energy / (kJ mol^{-1})	**Structure:**	**x / Å**	**y / Å**	**z / Å**		**Frequency / (cm^{-1})**
5.30	C	0.0000	0.0000	0	1	61
	H	1.1025	0.0000	0	2	102
	H	-0.3375	1.0484	0	3	141
	H	-0.3366	-0.4639	0.94192	4	182
	C	-0.5454	-0.7655	-1.21085	5	245
	H	-1.6493	-0.7349	-1.20501	6	378
	H	-0.2207	-0.2735	-2.14383	7	404
	C	-0.0876	-2.2302	-1.23381	8	416
	H	1.0191	-2.2726	-1.23691	9	732
	H	-0.3958	-2.7153	-0.28084	10	848
	C	-0.6196	-3.0107	-2.39822	11	880
	H	-1.5926	-2.7236	-2.80974	12	944
	C	-0.0859	-4.3794	-2.69705	13	969
	H	1.0177	-4.3834	-2.69488	14	1045
	H	-0.4308	-4.7501	-3.67416	15	1079
	H	-0.4068	-5.1166	-1.93272	16	1095
					17	1152
					18	1180
					19	1240
					20	1266
					21	1311
					22	1353

					23	1388
					24	1395
					25	1425
					26	1452
					27	1467
					28	1476
					29	1480
					30	1490
					31	1495
					32	2970
					33	3006
					34	3045
					35	3055
					36	3058
					37	3092
					38	3109
					39	3144
					40	3150
					41	3152
					42	3208
					ZPE	383.27 **kJ/mol**

pent-3-yl						
MP2	**aug-cc-pVDZ**					
Energy / (kJ mol^{-1})	**Structure:**	**x / Å**	**y / Å**	**z/ Å**		**Frequency / (cm^{-1})**
6.20	C	2.5169	-0.4047	-0.0816	1	52
	H	2.5778	-1.0567	0.8047	2	74
	H	3.4569	0.165	-0.1484	3	175
	H	2.4411	-1.0485	-0.9721	4	242
	C	1.3034	0.5295	0.0165	5	246
	H	1.4296	1.2001	0.8934	6	393
	H	1.2711	1.2006	-0.8621	7	401
	C	0.0000	-0.204	0.1259	8	411
	H	0.0000	-1.1953	0.5945	9	747
	C	-1.3034	0.5295	0.0165	10	782
	H	-1.2711	1.2006	-0.8621	11	880
	H	-1.4296	1.2001	0.8934	12	957
	C	-2.5169	-0.4047	-0.0816	13	1015
	H	-2.5778	-1.0567	0.8047	14	1050
	H	-3.4569	0.165	-0.1484	15	1072
	H	-2.4411	-1.0485	-0.9721	16	1084
					17	1153

					18	1176
					19	1256
					20	1270
					21	1273
					22	1349
					23	1392
					24	1396
					25	1432
					26	1454
					27	1465
					28	1489
					29	1489
					30	1494
					31	1494
					32	2986
					33	2989
					34	3060
					35	3061
					36	3061
					37	3062
					38	3150
					39	3150
					40	3156
					41	3156
					42	3188
					ZPE	**383.88 kJ/mol**

Entrance channel complex

pentane + Cl 1 pos						
Level	**SCS-MP2-F12/aug-cc-pVDZ//MP2/6-31G(d,p)**					
Energy / (kJ mol^{-1})	**Structure:**	**x / Å**	**y / Å**	**z / Å**		**Frequency / (cm^{-1})**
-6.00	C	4.0240	-0.9188	0.0000	1	13
	H	3.8643	-1.5414	0.8805	2	44
	H	5.0656	-0.5997	0.0000	3	67
	H	3.8643	-1.5414	-0.8805	4	117
	C	3.0745	0.2737	0.0000	5	126
	H	3.2701	0.8991	0.8749	6	185
	H	3.2701	0.8991	-0.8749	7	259
	C	1.6062	-0.1393	0.0000	8	278
	H	1.4076	-0.7652	0.8757	9	407
	H	1.4076	-0.7652	-0.8757	10	411
	C	0.6445	1.0442	0.0000	11	749

	H	0.8437	1.6682	-0.8751	12	791
	H	0.8437	1.6682	0.8751	13	904
	C	-0.8193	0.6163	0.0000	14	907
	H	-1.0444	0.0154	0.8817	15	964
	H	-1.4849	1.4791	0.0000	16	1037
	H	-1.0444	0.0154	-0.8817	17	1079
	Cl	-4.2025	-0.3934	0.0000	18	1093
					19	1123
					20	1203
					21	1272
					22	1322
					23	1334
					24	1369
					25	1372
					26	1409
					27	1454
					28	1459
					29	1466
					30	1542
					31	1545
					32	1556
					33	1560
					34	1566
					35	1571
					36	2128
					37	3100
					38	3114
					39	3119
					40	3120
					41	3124
					42	3147
					43	3167
					44	3179
					45	3218
					46	3220
					47	3220
					48	3267
					ZPE	**440.70 kJ/mol**

pentane + Cl 2 pos						
Level	**SCS-MP2-F12/aug-cc-pVDZ//MP2/6-31G(d,p)**					
Energy / (kJ mol^{-1})	**Structure:**	**x / Å**	**y / Å**	**z / Å**		**Frequency / (cm^{-1})**
	C	2.3955	-1.9443	0.0001	1	24

	H	3.0039	-1.7361	-0.8802	2	55
	H	2.1578	-3.0074	-0.0003	3	80
	H	3.0030	-1.7366	0.8812	4	119
	C	1.1328	-1.0901	-0.0003	5	124
	H	0.5252	-1.3347	-0.8757	6	179
	H	0.5244	-1.3351	0.8745	7	257
	C	1.4291	0.4062	0.0002	8	268
	H	2.0375	0.6540	-0.8754	9	405
	H	2.0367	0.6536	0.8763	10	408
	C	0.1743	1.2734	-0.0002	11	752
	H	-0.4301	1.0261	0.8775	12	792
	H	-0.4294	1.0262	-0.8784	13	892
	C	0.4806	2.7669	0.0001	14	904
	H	1.0612	3.0420	-0.8806	15	963
	H	-0.4321	3.3617	-0.0001	16	1022
	H	1.0608	3.0418	0.8810	17	1078
	Cl	-2.8113	-0.7134	0.0001	18	1094
					19	1123
					20	1202
					21	1256
					22	1313
					23	1323
					24	1368
					25	1373
					26	1411
					27	1455
					28	1462
					29	1466
					30	1538
					31	1541
					32	1553
					33	1560
					34	1560
					35	1564
					36	1568
					37	3099
					38	3108
					39	3116
					40	3123
					41	3124
					42	3145
					43	3166
					44	3179
					45	3217

					46	3218
					47	3220
					48	3220
					ZPE	**436.57 kJ/mol**

pentane + Cl 3 pos						
Level	**SCS-MP2-F12/aug-cc-pVDZ//MP2/6-31G(d,p)**					
Energy / (kJ mol^{-1})	**Structure:**	**x / Å**	**y / Å**	**z / Å**		**Frequency / (cm^{-1})**
-2.26	C	0.7807	-2.5382	0.0000	1	11
	H	0.1389	-2.5736	0.8806	2	16
	H	1.3992	-3.4351	-0.0001	3	26
	H	0.1387	-2.5736	-0.8805	4	109
	C	1.6311	-1.2731	0.0000	5	116
	H	2.2861	-1.2696	0.8751	6	182
	H	2.2859	-1.2696	-0.8753	7	255
	C	0.7938	0.0019	0.0000	8	264
	H	0.1406	-0.0004	0.8795	9	405
	H	0.1404	-0.0004	-0.8793	10	408
	C	1.6224	1.2825	0.0000	11	746
	H	2.2772	1.2835	-0.8752	12	785
	H	2.2773	1.2836	0.8752	13	890
	C	0.7632	2.5419	0.0000	14	905
	H	0.1211	2.5727	0.8805	15	963
	H	1.3756	3.4429	0.0001	16	1019
	H	0.1212	2.5728	-0.8806	17	1078
	Cl	-2.7206	-0.0072	0.0000	18	1093
					19	1123
					20	1202
					21	1253
					22	1310
					23	1324
					24	1366
					25	1370
					26	1409
					27	1456
					28	1463
					29	1467
					30	1540
					31	1546
					32	1555
					33	1559
					34	1560
					35	1567

					36	1570
					37	3101
					38	3113
					39	3118
					40	3123
					41	3123
					42	3145
					43	3163
					44	3177
					45	3216
					46	3217
					47	3219
					48	3219
					ZPE	**435.54 kJ/mol**

Exit channel complex

pent-1-yl + HCl						
Level	**SCS-MP2-F12/aug-cc-pVDZ//MP2/6-31G(d,p)**					
Energy / (kJ mol^{-1})	**Structure:**	**x / Å**	**y / Å**	**z / Å**		**Frequency / (cm^{-1})**
-2.26	C	3.044354	-1.265266	0.243785	1	32
	H	3.336666	-0.991729	1.257723	2	39
	H	3.945835	-1.540135	-0.30237	3	89
	H	2.407599	-2.147584	0.306835	4	124
	C	2.31003	-0.116105	-0.43719	5	141
	H	2.973122	0.749539	-0.51645	6	187
	H	2.050638	-0.401105	-1.46005	7	241
	C	1.041051	0.291365	0.303699	8	262
	H	1.296238	0.584907	1.326419	9	395
	H	0.376677	-0.572686	0.384658	10	405
	C	0.295613	1.44019	-0.37517	11	414
	H	0.030617	1.155322	-1.39713	12	430
	H	0.980674	2.293746	-0.47724	13	640
	C	-0.92568	1.875745	0.361885	14	749
	H	-0.91997	1.883468	1.443425	15	803
	H	-1.66246	2.499106	-0.12501	16	893
	H	-2.12175	0.083687	0.141904	17	947
	Cl	-2.78153	-0.997183	-0.06852	18	977
					19	1067
					20	1106
					21	1127
					22	1143
					23	1210

					24	1277
					25	1320
					26	1351
					27	1372
					28	1408
					29	1454
					30	1466
					31	1522
					32	1533
					33	1544
					34	1555
					35	1560
					36	1568
					37	2890
					38	3061
					39	3110
					40	3118
					41	3125
					42	3144
					43	3160
					44	3181
					45	3219
					46	3223
					47	3236
					48	3350
					ZPE	**419.71 kJ/mol**

pent-2-yl + HCl						
Level	**SCS-MP2-F12/aug-cc-pVDZ//MP2/6-31G(d,p)**					
Energy / (kJ mol^{-1})	**Structure:**	**x / Å**	**y / Å**	**z / Å**		**Frequency / (cm^{-1})**
-15.95	C	-2.95164	-0.969407	-0.26433	1	37
	H	-2.714444	-1.273553	-1.28376	2	55
	H	-3.393452	-1.824242	0.245617	3	79
	H	-3.704804	-0.182928	-0.31661	4	106
	C	-1.702877	-0.478902	0.458229	5	126
	H	-1.955034	-0.201642	1.484785	6	169
	H	-0.97369	-1.288732	0.523991	7	210
	C	-1.058488	0.71976	-0.23609	8	258
	H	-0.797717	0.453504	-1.26597	9	399
	H	-1.804552	1.524034	-0.32391	10	411
	C	0.151478	1.250267	0.461722	11	476
	H	0.152966	1.212312	1.546416	12	486

	H	1.408254	-0.348317	0.208722	13	594
	C	1.005771	2.283395	-0.19536	14	758
	H	1.215767	2.017786	-1.23183	15	884
	H	1.952948	2.417028	0.324653	16	906
	H	0.500399	3.25588	-0.20995	17	967
	Cl	2.202817	-1.32893	-0.0616	18	1018
					19	1079
					20	1107
					21	1148
					22	1176
					23	1215
					24	1295
					25	1319
					26	1365
					27	1413
					28	1457
					29	1467
					30	1475
					31	1524
					32	1539
					33	1546
					34	1551
					35	1560
					36	1566
					37	2776
					38	3048
					39	3087
					40	3123
					41	3125
					42	3129
					43	3177
					44	3181
					45	3219
					46	3224
					47	3225
					48	3245
					ZPE	**420.48 kJ/mol**

pent-3-yl + HCl						
Level	**SCS-MP2-F12/aug-cc-pVDZ//MP2/6-31G(d,p)**					
Energy / (kJ mol^{-1})	**Structure:**	**x / Å**	**y / Å**	**z / Å**		**Frequency / (cm^{-1})**
-15.94	C	2.51618	0.74119	0.344209	1	54

	H	2.564717	1.205961	1.328639	2	59
	H	3.437261	0.978637	-0.18552	3	77
	H	2.474816	-0.338068	0.481332	4	78
	C	1.297272	1.238965	-0.42779	5	144
	H	1.394292	2.319644	-0.603	6	184
	H	1.271745	0.78528	-1.42288	7	258
	C	-0.000409	0.978893	0.267403	8	265
	H	-0.000425	1.029644	1.353252	9	405
	H	0.000444	-1.048435	0.139302	10	414
	C	-1.298287	1.237997	-0.42778	11	487
	H	-1.27241	0.784369	-1.42288	12	506
	H	-1.396138	2.318608	-0.60294	13	590
	C	-2.516806	0.739245	0.3442	14	773
	H	-2.565706	1.203939	1.328649	15	824
	H	-3.438072	0.975994	-0.18552	16	907
	H	-2.474596	-0.339986	0.481279	17	981
	Cl	0.000963	-2.323137	-0.07595	18	1051
					19	1081
					20	1094
					21	1147
					22	1173
					23	1213
					24	1306
					25	1319
					26	1327
					27	1407
					28	1466
					29	1470
					30	1476
					31	1523
					32	1533
					33	1560
					34	1560
					35	1565
					36	1565
					37	2744
					38	3061
					39	3064
					40	3132
					41	3133
					42	3138
					43	3141
					44	3224
					45	3226

					46	3228
					47	3234
					48	3234
					ZPE	**421.10 kJ/mol**

Transition state

pent-1-yl + HCl TS						
Level	**SCS-MP2-F12/aug-cc-pVDZ//MP2/6-31G(d,p)**					
Energy / (kJ mol^{-1})	**Structure:**	**x / Å**	**y / Å**	**z / Å**		**Frequency / (cm^{-1})**
16.02	C	3.198587	-0.992914	0.225262	imag	-1066
	H	3.428085	-0.717012	1.259456	1	54
	H	4.144013	-1.105035	-0.313088	2	63
	H	2.698341	-1.966233	0.239695	3	125
	C	2.305149	0.060732	-0.429223	4	159
	H	2.827164	1.025663	-0.455284	5	184
	H	2.10625	-0.218937	-1.471138	6	262
	C	0.973593	0.229629	0.301663	7	399
	H	1.16459	0.514546	1.345076	8	410
	H	0.447315	-0.731956	0.324927	9	451
	C	0.069758	1.278561	-0.347275	10	527
	H	-0.117134	1.016399	-1.395404	11	739
	H	0.590542	2.249739	-0.358527	12	780
	C	-1.240529	1.469526	0.365663	13	880
	H	-1.198927	1.521129	1.454436	14	897
	H	-1.953159	2.161611	-0.082848	15	960
	H	-1.903688	0.298222	0.19002	16	971
	Cl	-2.592515	-0.960079	-0.084345	17	1023
					18	1052
					19	1089
					20	1120
					21	1146
					22	1213
					23	1248
					24	1289
					25	1323
					26	1356
					27	1373
					28	1411
					29	1456
					30	1467
					31	1513
					32	1524

					33	1545
					34	1555
					35	1560
					36	1568
					37	3078
					38	3111
					39	3119
					40	3126
					41	3158
					42	3164
					43	3185
					44	3193
					45	3220
					46	3224
					47	3296
					ZPE	**416.10 kJ/mol**

pent-2-yl + HCl TS						
Level	**SCS-MP2-F12/aug-cc-pVDZ//MP2/6-31G(d,p)**					
Energy / (kJ mol^{-1})	**Structure:**	**x / Å**	**y / Å**	**z / Å**		**Frequency / (cm^{-1})**
-0.18	C	3.060466	-0.550369	-0.254226	imag	-930
	H	2.913675	-0.841458	-1.299028	1	66
	H	3.649322	-1.331509	0.23431	2	82
	H	3.645625	0.374878	-0.239918	3	131
	C	1.71502	-0.353906	0.443702	4	154
	H	1.150945	-1.292618	0.435576	5	185
	H	1.876585	-0.085848	1.495008	6	224
	C	0.873176	0.734785	-0.222726	7	258
	H	0.711668	0.489811	-1.280545	8	394
	H	1.42762	1.687779	-0.205882	9	413
	C	-0.46141	0.973463	0.437881	10	515
	H	-0.4237	0.985009	1.531688	11	742
	H	-1.10869	-0.153294	0.244272	12	799
	C	-1.3663	2.014436	-0.170172	13	882
	H	-1.48254	1.845515	-1.244094	14	907
	H	-2.35463	2.007782	0.295365	15	962
	H	-0.92669	3.010237	-0.026566	16	977
	Cl	-1.88264	-1.388631	-0.079232	17	1044
					18	1068
					19	1097
					20	1123

					21	1172
					22	1216
					23	1252
					24	1308
					25	1318
					26	1369
					27	1411
					28	1454
					29	1463
					30	1468
					31	1518
					32	1539
					33	1546
					34	1551
					35	1560
					36	1566
					37	3072
					38	3112
					39	3125
					40	3127
					41	3149
					42	3187
					43	3192
					44	3205
					45	3220
					46	3226
					47	3242
					ZPE	**416.27 kJ/mol**

pent-3-yl + HCl TS						
Level	**SCS-MP2-F12/aug-cc-pVDZ//MP2/6-31G(d,p)**					
Energy / (kJ mol^{-1})	**Structure:**	**x / Å**	**y / Å**	**z / Å**		**Frequency / (cm^{-1})**
-1.69	C	-2.538588	-0.642362	0.333437	imag	-881
	H	-2.555844	-1.033916	1.35522	1	83
	H	-3.448509	-0.974337	-0.173351	2	95
	H	-2.553353	0.44912	0.383543	3	113
	C	-1.294041	-1.129237	-0.409104	4	139
	H	-1.303255	-2.228498	-0.473172	5	191
	H	-1.292599	-0.757389	-1.440418	6	261
	C	-0.000106	-0.731443	0.256694	7	263
	H	-0.000167	-0.845111	1.346855	8	409
	H	0.000082	0.592212	0.161521	9	410
	C	1.293758	-1.129653	-0.408982	10	518

	H	1.292365	-0.758156	-1.440422	11	743
	H	1.302783	-2.228939	-0.472675	12	770
	C	2.538404	-0.642766	0.333387	13	894
	H	2.555531	-1.033891	1.355337	14	912
	H	3.448254	-0.97519	-0.173233	15	944
	H	2.553443	0.448732	0.383036	16	984
	Cl	0.000277	2.058713	-0.08499	17	1062
					18	1068
					19	1086
					20	1111
					21	1166
					22	1216
					23	1245
					24	1308
					25	1317
					26	1348
					27	1408
					28	1462
					29	1466
					30	1470
					31	1517
					32	1528
					33	1559
					34	1559
					35	1567
					36	1567
					37	3084
					38	3089
					39	3134
					40	3134
					41	3161
					42	3161
					43	3181
					44	3227
					45	3227
					46	3241
					47	3241
					ZPE	**416.54 kJ/mol**

S.5 Geometries and frequencies of the stationary points from the *EVB* fit

Reactants and Products

pentane						
Level	EVB					
Energy / (kJ mol^{-1})	Structure	x / Å	y / Å	z/ Å		Frequency / (cm^{-1})
-2.04	C	2.5385	-0.3351	0.0000	1	100
	H	2.5760	-0.9827	0.8894	2	118
	H	3.4430	0.2924	0.0000	3	237
	H	2.5760	-0.9827	-0.8894	4	247
	C	1.2731	0.5212	0.0000	5	248
	H	1.2683	1.1776	0.8837	6	378
	H	1.2683	1.1776	-0.8837	7	477
	C	0.0000	-0.3224	0.0000	8	685
	H	0.0000	-0.9808	0.8824	9	753
	H	0.0000	-0.9808	-0.8824	10	764
	C	-1.2731	0.5212	0.0000	11	874
	H	-1.2683	1.1776	-0.8837	12	899
	H	-1.2683	1.1776	0.8837	13	905
	C	-2.5385	-0.3351	0.0000	14	937
	H	-2.5759	-0.9827	0.8894	15	955
	H	-3.4430	0.2924	0.0000	16	983
	H	-2.5760	-0.9827	-0.8894	17	987
					18	1157
					19	1185
					20	1247
					21	1248
					22	1287
					23	1374
					24	1418
					25	1427
					26	1475
					27	1475
					28	1477
					29	1495
					30	1516
					31	1522
					32	1555
					33	1596
					34	2866
					35	2949
					36	3168
					37	3177

					38	3206
					39	3207
					40	3219
					41	3228
					42	3276
					43	3283
					44	3285
					45	3286
					ZPE	**425.58 kJ/mol**

pent-1-yl						
Level	**EVB**					
Energy / (kJ mol^{-1})	**Structure**	**x / Å**	**y / Å**	**z/ Å**		**Frequency / (cm^{-1})**
-1.42	C	2.5076	-0.2720	0.0741	1	29
	H	2.5357	-0.9330	0.9540	2	109
	H	3.3922	0.3820	0.1142	3	139
	H	2.5944	-0.9032	-0.8236	4	243
	C	1.2174	0.5463	0.0453	5	247
	H	1.1650	1.1877	0.9385	6	386
	H	1.2229	1.2171	-0.8276	7	466
	C	-0.0299	-0.3346	-0.0100	8	580
	H	-0.0383	-1.0073	0.8616	9	735
	H	0.0187	-0.9779	-0.9022	10	752
	C	-1.3281	0.4702	-0.0383	11	842
	H	-1.3104	1.1423	-0.9100	12	867
	H	-1.3649	1.1157	0.8527	13	896
	C	-2.5496	-0.3942	-0.0888	14	911
	H	-2.4838	-1.4589	0.1391	15	968
	H	-3.5421	0.0478	-0.1846	16	971
					17	1078
					18	1162
					19	1170
					20	1236
					21	1247
					22	1288
					23	1372
					24	1404
					25	1449
					26	1473
					27	1483
					28	1511
					29	1520
					30	1572

					31	1674
					32	2730
					33	2890
					34	2999
					35	3139
					36	3183
					37	3207
					38	3217
					39	3223
					40	3247
					41	3277
					42	3283
					ZPE	**383.83 kJ/mol**

pent-2-yl						
Level	**EVB**					
Energy / (kJ mol^{-1})	**Structure**	**x / Å**	**y / Å**	**z/ Å**		**Frequency / (cm^{-1})**
-1.32	C	2.5335	-0.3299	0.0057	1	88
	H	2.6001	-0.8499	-0.9624	2	126
	H	3.4301	0.2997	0.1129	3	190
	H	2.5599	-1.0925	0.7992	4	229
	C	1.2576	0.5075	0.0922	5	241
	H	1.2258	1.0371	1.0568	6	391
	H	1.2652	1.2786	-0.6935	7	451
	C	-0.0066	-0.3379	-0.0527	8	572
	H	0.0241	-0.8699	-1.0161	9	719
	H	-0.0122	-1.1139	0.7283	10	766
	C	-1.2699	0.4630	0.0335	11	843
	H	-1.2209	1.4541	0.4959	12	893
	C	-2.5994	-0.2156	-0.0910	13	916
	H	-2.6930	-0.7281	-1.0608	14	919
	H	-3.4253	0.5078	-0.0119	15	973
	H	-2.7351	-0.9688	0.7003	16	1047
					17	1086
					18	1187
					19	1205
					20	1232
					21	1279
					22	1370
					23	1407
					24	1419
					25	1469
					26	1472

					27	1477
					28	1510
					29	1532
					30	1577
					31	1774
					32	2839
					33	2878
					34	2986
					35	3073
					36	3179
					37	3194
					38	3214
					39	3265
					40	3278
					41	3282
					42	3285
					ZPE	**387.78 kJ/mol**

pent-3-yl						
Level	**EVB**					
Energy / (kJ mol^{-1})	**Structure**	**x / Å**	**y / Å**	**z/ Å**		**Frequency / (cm^{-1})**
-1.76	C	2.5177	-0.4122	0.0408	1	88
	H	2.5079	-1.0051	0.9684	2	92
	H	3.4602	0.1557	0.0121	3	218
	H	2.5198	-1.1146	-0.8068	4	254
	C	1.3089	0.5200	-0.0249	5	270
	H	1.3453	1.2300	0.8156	6	398
	H	1.3572	1.1213	-0.9457	7	449
	C	0.0051	-0.2169	0.0118	8	622
	H	-0.0021	-1.2432	0.3984	9	665
	C	-1.2927	0.5288	-0.0495	10	798
	H	-1.3194	1.1304	-0.9710	11	824
	H	-1.3401	1.2392	0.7901	12	895
	C	-2.5089	-0.3951	-0.0067	13	913
	H	-2.5207	-0.9878	0.9209	14	968
	H	-3.4468	0.1793	-0.0532	15	975
	H	-2.4998	-1.0975	-0.8542	16	986
					17	1112
					18	1170
					19	1219
					20	1223
					21	1242
					22	1354

					23	1415
					24	1453
					25	1472
					26	1477
					27	1479
					28	1526
					29	1531
					30	1563
					31	1782
					32	2858
					33	2937
					34	2955
					35	3125
					36	3179
					37	3187
					38	3230
					39	3239
					40	3280
					41	3283
					42	3285
					ZPE	**388.74 kJ/mol**

Entrance channel complex

pentane + Cl 1 pos						
Level	**EVB**					
Energy / (kJ mol^{-1})	**Structure:**	**x / Å**	**y / Å**	**z / Å**		**Frequency / (cm^{-1})**
-5.69	C	4.33076	0.41129	0.00001	1	3
	H	4.36548	-0.23769	0.89061	2	15
	H	5.23927	1.03412	0.00002	3	39
	H	4.36549	-0.23769	-0.89059	4	102
	C	3.05926	1.26824	0	5	119
	H	3.05661	1.9295	0.88504	6	246
	H	3.05662	1.9295	-0.88505	7	248
	C	1.77962	0.42465	0	8	251
	H	1.77962	-0.23863	0.88559	9	379
	H	1.77961	-0.23861	-0.88562	10	503
	C	0.49998	1.26824	0.00001	11	766
	H	0.50262	1.92951	-0.88502	12	804
	H	0.50262	1.92949	0.88506	13	853
	C	-0.77152	0.41129	0.00001	14	900
	H	-0.80624	-0.23771	0.89059	15	906
	H	-1.68003	1.03412	0.00002	16	909

	H	-0.80625	-0.23768	-0.8906	17	938
	Cl	-3.66093	-1.53608	-0.00001	18	1037
					19	1055
					20	1084
					21	1157
					22	1217
					23	1247
					24	1248
					25	1343
					26	1427
					27	1475
					28	1475
					29	1478
					30	1478
					31	1485
					32	1496
					33	1516
					34	1523
					35	1555
					36	1599
					37	3168
					38	3168
					39	3207
					40	3212
					41	3219
					42	3276
					43	3280
					44	3283
					45	3286
					46	3286
					47	3286
					48	3287
					ZPE	**435.64 kJ/mol**

pentane + Cl 2 pos						
Level	**EVB**					
Energy / (kJ mol^{-1})	**Structure:**	**x / Å**	**y / Å**	**z / Å**		**Frequency / (cm^{-1})**
-9.02	C	2.395	-1.7003	0	1	28
	H	2.42972	-2.34928	0.8906	2	37
	H	3.30351	-1.07747	0	3	48
	H	2.42974	-2.34928	-0.8906	4	101
	C	1.1235	-0.84335	-0.00002	5	125
	H	1.12086	-0.18209	0.88502	6	246

	H	1.12087	-0.1821	-0.88507	7	247
	C	-0.15614	-1.68695	-0.00002	8	252
	H	-0.15613	-2.35022	0.88558	9	378
	H	-0.15614	-2.3502	-0.88563	10	503
	C	-1.43577	-0.84335	0	11	768
	H	-1.43314	-0.18208	-0.88504	12	809
	H	-1.43313	-0.1821	0.88505	13	853
	C	-2.70728	-1.7003	-0.00001	14	900
	H	-2.742	-2.3493	0.89058	15	906
	H	-3.61578	-1.07747	0.00001	16	909
	H	-2.74201	-2.34927	-0.89062	17	937
	Cl	0.32121	2.80777	0.00003	18	1036
					19	1055
					20	1084
					21	1157
					22	1218
					23	1248
					24	1249
					25	1343
					26	1427
					27	1475
					28	1475
					29	1478
					30	1478
					31	1486
					32	1496
					33	1516
					34	1523
					35	1556
					36	1599
					37	3168
					38	3168
					39	3207
					40	3213
					41	3220
					42	3277
					43	3281
					44	3283
					45	3285
					46	3286
					47	3287
					48	3288
					ZPE	**436.08 kJ/mol**

pentane + Cl 3 pos						
Level	EVB					
Energy / (kJ mol^{-1})	Structure:	x / Å	y / Å	z / Å		Frequency / (cm^{-1})
-9.26	C	2.08959	0.90315	0.00003	1	20
	H	2.12431	0.25417	0.89063	2	34
	H	2.9981	1.52598	0.00003	3	49
	H	2.12433	0.25417	-0.89057	4	105
	C	0.81809	1.7601	0.00001	5	121
	H	0.81545	2.42136	0.88505	6	248
	H	0.81546	2.42135	-0.88504	7	250
	C	-0.46155	0.9165	0.00001	8	257
	H	-0.46154	0.25323	0.88561	9	378
	H	-0.46155	0.25325	-0.8856	10	503
	C	-1.74118	1.7601	0.00003	11	770
	H	-1.73855	2.42137	-0.88501	12	804
	H	-1.73854	2.42135	0.88508	13	853
	C	-3.01269	0.90315	0.00002	14	902
	H	-3.04741	0.25415	0.89061	15	906
	H	-3.92119	1.52598	0.00004	16	909
	H	-3.04742	0.25418	-0.89059	17	937
	Cl	0.94947	-2.5479	-0.00004	18	1036
					19	1054
					20	1083
					21	1158
					22	1217
					23	1247
					24	1249
					25	1342
					26	1427
					27	1475
					28	1475
					29	1478
					30	1478
					31	1485
					32	1497
					33	1518
					34	1523
					35	1555
					36	1599
					37	3168
					38	3169
					39	3208

					40	3212
					41	3220
					42	3277
					43	3280
					44	3283
					45	3286
					46	3286
					47	3286
					48	3288
					ZPE	**436.05 kJ/mol**

Exit channel complex

pent-1-yl + HCl						
Level	**EVB**					
Energy / (kJ mol^{-1})	**Structure:**	**x / Å**	**y / Å**	**z / Å**		**Frequency / (cm^{-1})**
-11.14	C	3.1792	0.1780	1.2160	1	35
	H	3.2158	-0.4839	2.0949	2	54
	H	4.0620	0.8348	1.2504	3	86
	H	3.2611	-0.4519	0.3169	4	114
	C	1.8863	0.9922	1.1976	5	143
	H	1.8378	1.6327	2.0917	6	202
	H	1.8835	1.6637	0.3252	7	226
	C	0.6424	0.1072	1.1494	8	247
	H	0.6381	-0.5627	2.0232	9	252
	H	0.6938	-0.5396	0.2604	10	266
	C	-0.6583	0.9079	1.1210	11	393
	H	-0.6367	1.5906	0.2578	12	481
	H	-0.7041	1.5426	2.0193	13	683
	C	-1.8764	0.0387	1.0505	14	785
	H	-1.8468	-0.9830	1.4329	15	886
	H	-2.8532	0.4698	0.8252	16	897
	H	-1.6203	-0.6818	-1.0692	17	904
	Cl	-1.3146	-0.8777	-2.3041	18	942
					19	1004
					20	1063
					21	1064
					22	1093
					23	1202
					24	1219
					25	1237
					26	1302
					27	1414

					28	1464
					29	1466
					30	1475
					31	1478
					32	1488
					33	1514
					34	1534
					35	1583
					36	1760
					37	2811
					38	2956
					39	3168
					40	3173
					41	3210
					42	3219
					43	3277
					44	3282
					45	3283
					46	3285
					47	3285
					48	3287
					ZPE	**419.86 kJ/mol**

pent-2-yl + HCl						
Level	**EVB**					
Energy / (kJ mol^{-1})	**Structure:**	**x / Å**	**y / Å**	**z / Å**		**Frequency / (cm^{-1})**
-22.88	C	-0.6674	1.8586	2.5307	1	31
	H	0.4143	1.8127	2.7301	2	33
	H	-0.9593	2.9194	2.4948	3	97
	H	-1.1864	1.3944	3.3834	4	107
	C	-1.0147	1.1466	1.2238	5	127
	H	-2.0956	1.2277	1.0321	6	170
	H	-0.5057	1.6445	0.3846	7	229
	C	-0.6226	-0.3298	1.2422	8	240
	H	0.4560	-0.4141	1.4465	9	251
	H	-1.1349	-0.8282	2.0796	10	261
	C	-0.9451	-1.0456	-0.0352	11	388
	H	-1.7426	-0.6332	-0.6626	12	498
	H	0.5261	-0.1500	-1.3110	13	744
	C	-0.5956	-2.4961	-0.1793	14	785
	H	0.4834	-2.6598	-0.0353	15	844
	H	-0.8627	-2.8731	-1.1784	16	859
	H	-1.1290	-3.1074	0.5647	17	903

	Cl	1.5394	0.3447	-1.9519	18	910
					19	951
					20	1008
					21	1065
					22	1098
					23	1162
					24	1203
					25	1239
					26	1247
					27	1342
					28	1404
					29	1460
					30	1475
					31	1478
					32	1491
					33	1512
					34	1520
					35	1572
					36	1673
					37	2899
					38	2956
					39	2999
					40	3168
					41	3209
					42	3213
					43	3221
					44	3277
					45	3280
					46	3284
					47	3285
					48	3287
					ZPE	**415.41 kJ/mol**

pent-3-yl + HCl						
Level	**EVB**					
Energy / (kJ mol^{-1})	**Structure:**	**x / Å**	**y / Å**	**z / Å**		**Frequency / (cm^{-1})**
-24.88	C	2.48188	0.07117	1.14208	1	44
	H	2.4757	-0.57289	2.03479	2	47
	H	3.41279	0.65848	1.15512	3	75
	H	2.50728	-0.58253	0.25697	4	95
	C	1.2553	0.98187	1.11714	5	157
	H	1.27055	1.64446	1.99606	6	209
	H	1.29862	1.63469	0.23184	7	231

	C	-0.03442	0.21783	1.1016	8	247
	H	-0.03407	-0.80078	1.50921	9	267
	H	0.0333	-0.59104	-0.91058	10	289
	C	-1.34061	0.95096	1.04221	11	399
	H	-1.3483	1.60318	0.15544	12	478
	H	-1.42226	1.6124	1.91833	13	670
	C	-2.54461	0.01137	0.99699	14	789
	H	-2.57462	-0.63298	1.88901	15	870
	H	-3.4884	0.57638	0.95591	16	873
	H	-2.50337	-0.64215	0.11233	17	914
	Cl	0.07321	-0.8773	-2.17442	18	984
					19	1009
					20	1039
					21	1066
					22	1108
					23	1203
					24	1221
					25	1224
					26	1272
					27	1453
					28	1470
					29	1478
					30	1480
					31	1480
					32	1483
					33	1525
					34	1533
					35	1562
					36	1771
					37	2826
					38	2954
					39	3169
					40	3169
					41	3214
					42	3216
					43	3279
					44	3280
					45	3286
					46	3286
					47	3287
					48	3287
					ZPE	**420.31 kJ/mol**

Transition State

pent-1-yl + HCl TS						
Level	EVB					
Energy / (kJ mol^{-1})	Structure:	x / Å	y / Å	z / Å		Frequency / (cm^{-1})
14.20	C	3.58E+00	-3.27E-01	2.70E-02	imag	-1660
	H	3.78E+00	-1.49E-01	1.10E+00	1	47
	H	4.52E+00	-1.68E-01	-5.23E-01	2	69
	H	3.29E+00	-1.38E+00	-9.03E-02	3	115
	C	2.47E+00	5.98E-01	-4.87E-01	4	168
	H	2.79E+00	1.65E+00	-3.86E-01	5	242
	H	2.31E+00	4.19E-01	-1.56E+00	6	250
	C	1.15E+00	4.05E-01	2.58E-01	7	381
	H	1.31E+00	5.97E-01	1.33E+00	8	401
	H	8.37E-01	-6.45E-01	1.70E-01	9	445
	C	4.31E-02	1.32E+00	-2.58E-01	10	507
	H	-1.36E-01	1.11E+00	-1.32E+00	11	760
	H	3.95E-01	2.36E+00	-2.03E-01	12	800
	C	-1.25E+00	1.18E+00	5.22E-01	13	856
	H	-1.16E+00	1.07E+00	1.61E+00	14	898
	H	-2.09E+00	1.80E+00	1.91E-01	15	908
	H	-1.78E+00	-3.32E-02	2.33E-01	16	917
	Cl	-2.48E+00	-1.30E+00	-3.79E-02	17	982
					18	1006
					19	1047
					20	1069
					21	1088
					22	1149
					23	1210
					24	1241
					25	1248
					26	1343
					27	1416
					28	1465
					29	1475
					30	1478
					31	1488
					32	1493
					33	1515
					34	1524
					35	1569
					36	1624
					37	3036
					38	3151

					39	3169
					40	3209
					41	3213
					42	3221
					43	3278
					44	3281
					45	3285
					46	3286
					47	3287
					ZPE	**416.34 kJ/mol**

pent-2-yl + HCl TS						
Level	**EVB**					
Energy / (kJ mol^{-1})	**Structure:**	**x / Å**	**y / Å**	**z / Å**		**Frequency / (cm^{-1})**
-4.55	C	2.35E+00	-2.13E+00	-1.71E-01	imag	-94
	H	2.43E+00	-2.03E+00	-1.26E+00	1	32
	H	3.34E+00	-1.94E+00	2.62E-01	2	57
	H	2.08E+00	-3.18E+00	4.75E-02	3	103
	C	1.31E+00	-1.17E+00	3.93E-01	4	135
	H	1.26E+00	-1.27E+00	1.49E+00	5	222
	H	1.61E+00	-1.31E-01	1.84E-01	6	229
	C	-8.30E-02	-1.41E+00	-1.92E-01	7	270
	H	-4.20E-02	-1.30E+00	-1.29E+00	8	341
	H	-3.86E-01	-2.45E+00	6.58E-03	9	444
	C	-1.14E+00	-4.61E-01	3.73E-01	10	505
	H	-1.18E+00	-5.71E-01	1.47E+00	11	628
	H	-8.29E-01	5.79E-01	1.72E-01	12	731
	C	-2.52E+00	-7.07E-01	-2.22E-01	13	817
	H	-2.51E+00	-5.78E-01	-1.32E+00	14	858
	H	-3.26E+00	-5.60E-03	1.92E-01	15	899
	H	-2.87E+00	-1.73E+00	-7.19E-03	16	910
	Cl	1.73E-01	2.75E+00	-6.88E-03	17	951
					18	993
					19	1038
					20	1087
					21	1131
					22	1221
					23	1246
					24	1251
					25	1282
					26	1317
					27	1375
					28	1455

					29	1476
					30	1479
					31	1489
					32	1512
					33	1523
					34	1550
					35	1583
					36	2792
					37	2883
					38	3013
					39	3135
					40	3160
					41	3193
					42	3208
					43	3231
					44	3253
					45	3269
					46	3278
					47	3293
					ZPE	**417.76 kJ/mol**

pent-3-yl + HCl TS						
Level	**EVB**					
Energy / (kJ mol^{-1})	**Structure:**	**x / Å**	**y / Å**	**z / Å**		**Frequency / (cm^{-1})**
-2.82	C	2.24E+00	1.26E+00	3.55E-01	imag	-1499
	H	2.18E+00	1.35E+00	1.45E+00	1	54
	H	3.02E+00	1.94E+00	-3.50E-03	2	83
	H	2.56E+00	2.32E-01	1.21E-01	3	120
	C	8.94E-01	1.57E+00	-2.97E-01	4	181
	H	6.55E-01	2.63E+00	-1.16E-01	5	222
	H	9.61E-01	1.46E+00	-1.39E+00	6	255
	C	-2.47E-01	7.23E-01	2.33E-01	7	284
	H	-2.67E-01	6.10E-01	1.33E+00	8	373
	H	6.66E-02	-5.61E-01	-2.42E-02	9	406
	C	-1.59E+00	1.07E+00	-3.79E-01	10	498
	H	-1.57E+00	9.09E-01	-1.47E+00	11	791
	H	-1.77E+00	2.15E+00	-2.39E-01	12	801
	C	-2.77E+00	3.21E-01	2.46E-01	13	871
	H	-2.81E+00	4.82E-01	1.33E+00	14	926
	H	-3.73E+00	6.72E-01	-1.74E-01	15	957
	H	-2.69E+00	-7.60E-01	5.91E-02	16	965
	Cl	5.92E-01	-2.02E+00	-3.47E-02	17	1005
					18	1028

					19	1064
					20	1090
					21	1126
					22	1172
					23	1220
					24	1246
					25	1295
					26	1445
					27	1470
					28	1472
					29	1480
					30	1482
					31	1484
					32	1497
					33	1527
					34	1557
					35	1589
					36	1637
					37	3109
					38	3169
					39	3173
					40	3203
					41	3206
					42	3273
					43	3274
					44	3281
					45	3286
					46	3294
					47	3295
					ZPE	**420.11 kJ/mol**

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