SUPPORTING INFORMATION

Quantum Tunnelling Dominates Chloride Leaching from Polyvinyl Chloride

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1. Computational Methods

In this section, we detail our methodology, including conformer search, basis set and functional benchmarking, computational model validation, and tunnelling calculations. We perform all density functional theory (DFT) calculations with Gaussian 16[1] and use ORCA 5.0.4[2] for domain-based local pair natural orbital coupled-cluster theory[3] (DLPNO-CCSD(T)) calculations. For the tunnelling calculations, we use Polyrate 17[4], with Gaussrate 17[5] as an interface between Gaussian 16 and Polyrate 17.

Conformer Search

We use the Conformer-Rotamer Ensemble Sampling Tool[6] (CREST) to determine the most stable conformer of all the reactants and products. We consider conformers within 6 kcal/mol of the lowest energy conformer at the GFN2-xTB[7] level of theory after metadynamics simulations with a 1.5 fs timestep.[8] We then optimize the generated conformers at the ωB97X-D(SMD=Water)/6-31+G(d,p)[9-14] level of theory and retain the lowest-energy structure. We confirm all stationary points by a normal mode analysis.

Benchmarking the Basis Set and Density Functional

We aim to accurately describe the potential energy surface of the studied reaction while maintaining reasonable computational cost. For this reason, we benchmark various DFT methods and basis sets on electronic energy barriers ($\Delta E^{\ddagger}$) using DLPNO-CCSD(T)/aug-cc-pVTZ//ωB97X-D/def2-QZVPPD[3, 13, 15, 16] as our reference. We compare three methods: M06-2X,[17] ωB97X-D,[13] and DLPNO-CCSD(T) with the "TightPNO" option.[3] M06-2X and ωB97X-D are known to perform relatively well on barrier heights,[18] while DLPNO-CCSD(T) has been shown to be of comparable accuracy to CCSD(T), the gold standard in quantum chemistry.[3, 19] We also evaluate seven basis sets: 6-31+G(d,p),[9, 12] 6-31++G(d,p),[10, 12, 14, 20] 6-311+G(d,p),[9, 20] 6-311++G(d,p),[9] def2-TZVPPD,[16, 21] aug-cc-pVTZ,[15, 22, 23] and def2-QZVPPD.[21, 24] We include solvation effects using the SMD model.[11] Sample input files can be found in Section 3B of the Supporting Information (SI). Our results in Table S1 show that the studied composite methods, DLPNO-CCSD(T)/aug-cc-pVTZ//ωB97X-D/def2-QZVPPD, DLPNO-CCSD(T)(SMD=Water)/def2-TZVPPD//ωB97X-D(SMD=Water)/6-311+G(d,p), and DLPNO-CCSD(T)(SMD=Water)/def2-TZVPPD//ωB97X-D(SMD=Water)/6-31+G(d,p), provide very similar energy barriers ($\Delta E^{\ddagger}$ = 19.8, 20.9, and 20.9 kcal/mol, respectively). We also find that the geometries calculated with the ωB97X-D functional do not change significantly with the various basis sets. To demonstrate that we mention the critical O-H bond length in the transition state is 1.255, 1.267, 1.256, 1.279, 1.279, 1.274, and 1.275 Å with def2-QZVPPD, aug-cc-pVTZ, def2-TZVPPD, 6-311++G(d,p), 6-311+G(d,p), 6-31++G(d,p), and 6-31+G(d,p), respectively. Overall, we conclude that ωB97X-D provides reasonable geometries for our system. Furthermore, we see that ωB97X-D also provides reasonable energetics with small basis set size where the error relative to our reference method is only -0.9, -1.7, -1.0, -1.9, -1.9, -1.6, and -1.6 kcal/mol (Table S1) when used with def2-QZVPPD, aug-cc-pVTZ, def2-TZVPPD, 6-311++G(d,p), 6-311+G(d,p), 6-31++G(d,p), and 6-31+G(d,p), respectively. Conversely, M06-2X(SMD=Water)/6-31+G(d,p) and M06-2X(SMD=Water)/6-311+G(d,p) perform relatively poorly with a relative error of -3.8 and -3.9 kcal/mol, respectively. Hence, we select ωB97X-D(SMD=Water)/6-311+G(d,p) for the tunnelling calculations. Finally, we note that ωB97X-D(SMD=Water)/6-311+G(d,p) underestimates the thermal barrier slightly and thus the contribution of quantum tunnelling to the chloride leaching rate is expected to be higher than indicated by the chosen level of theory.[25]

Table S1. Electronic energy barriers ($\Delta E^{\ddagger}$) for chloride leaching from the two monomer-unit model at different levels of theory. $\Delta E^{\ddagger}_{rel}$ represents the difference in $\Delta E^{\ddagger}$ given by each method and that given by DLPNO-CCSD(T)(SMD=Water)/aug-cc-pVTZ//ωB97X-D(SMD=Water)/def2-QZVPPD.

Method	$\Delta E^{\ddagger}$ **(kcal/mol)**	$\Delta E^{\ddagger}_{rel}$ **(kcal/mol)**
DLPNO-CCSD(T)(SMD=Water)/aug-cc-pVTZ//ωB97X-D(SMD=Water)/def2-QZVPPD	19.8	0.0
DLPNO-CCSD(T)(SMD=Water)/def2-TZVPPD//ωB97X-D(SMD=Water)/6-311+G(d,p)	20.9	0.9
DLPNO-CCSD(T)(SMD=Water)/def2-TZVPPD//ωB97X-D(SMD=Water)/6-31+G(d,p)	20.9	0.9
ωB97X-D(SMD=Water)/def2-QZVPPD	18.9	-0.9
ωB97X-D(SMD=Water)/def2-TZVPPD	18.8	-1.0
ωB97X-D(SMD=Water)/6-31++G(d,p)	18.2	-1.6
ωB97X-D(SMD=Water)/6-31+G(d,p)	18.2	-1.6
ωB97X-D(SMD=Water)/aug-cc-pVTZ	18.1	-1.7
ωB97X-D(SMD=Water)/6-311++G(d,p)	17.9	-1.9
ωB97X-D(SMD=Water)/6-311+G(d,p)	17.9	-1.9
M06-2X(SMD=Water)/6-31+G(d,p)	16.0	-3.8
M06-2X(SMD=Water)/6-311+G(d,p)	15.9	-3.9

Benchmarking the Computational Model

We also investigate the convergence of $\Delta E^{\ddagger}$, the reaction energy (ΔE_R), and the transition state imaginary frequency (ν_i) with respect to the number of monomer units used in the computational model. We select $\Delta E^{\ddagger}$, ΔE_R, and ν_i as they are strongly related to quantum tunnelling due to the dependence of tunnelling probabilities on barrier height and width.[26, 27] We calculate the chosen parameters for models containing 2, 3, 4, and 5 monomer units. Sample input files can be found in Section 3B of this document. We present our results in Table S2. We observe minimal variation in $\Delta E^{\ddagger}$, ΔE_R, and ν_i as function of model size at ωB97X-D(SMD=Water)/def2-TZVPPD level of theory. ν_I is 1501, 1520, 1490, and 1531 cm^{-1} for the 2, 3, 4, and 5 monomer-unit models, respectively. $\Delta E^{\ddagger}$ is also relatively consistent with values of 18.8, 19.2, 18.5, and 19.1 kcal/mol for the 2, 3, 4, and 5 monomer-unit models, respectively. The same consistency is observed in ΔE_R (Table S2). Using ωB97X-D(SMD=Water)/6-311+G(d,p), we also observe minimal variation in $\Delta E^{\ddagger}$, ΔE_R, and ν_i and what is more important, results are in agreement with the ωB97X-D(SMD=Water)/def2-TZVPPD results (Table S2). ν_i changes non-monotonically between 1491 and 1524 cm^{-1} for the 2 and 5 monomer-unit models, respectively. $\Delta E^{\ddagger}$ is also consistent with values of 17.9, 17.6, 17.2, and 17.8 kcal/mol for the 2, 3, 4, and 5 monomer-unit models, respectively. ΔE_R changes marginally, at 20.6, 19.5, 19.2, and 19.7 kcal/mol for the 2, 3, 4, and 5 monomer-unit models, respectively. Finally, we also see a similar trend with ωB97X-D(SMD=Water)/6-31+G(d,p) (Table S2). Given the negligible variations in $\Delta E^{\ddagger}$, ΔE_R, and ν_i on all three levels of theory used, we infer that tunnelling probabilities are likely to be similar across the different models. Consequently, we select the 2 monomer-unit model for subsequent tunnelling calculations due to computational cost reasons.

Table S2. Computed reaction energy (ΔE_R), electronic energy barrier ($\Delta E^{\ddagger}$), enthalpy barrier ($\Delta H^{\ddagger}$), and free energy barrier ($\Delta G^{\ddagger}$) in kcal/mol, as well as the transition state imaginary frequency (ν_i) in cm^{-1} for chloride leaching from the 2, 3, 4, and 5 monomer-unit models.

	ωB97X-D(SMD=Water)/6-31+G(d,p)					*ωB97X-D(SMD=Water)/def2-TZVPPD*					*ωB97X-D(SMD=Water)/6-311+G(d,p)*				
	ΔE_R	$\Delta E^{\ddagger}$	$\Delta H^{\ddagger}$	$\Delta G^{\ddagger}$	ν_i	ΔE_R	$\Delta E^{\ddagger}$	$\Delta H^{\ddagger}$	$\Delta G^{\ddagger}$	ν_i	ΔE_R	$\Delta E^{\ddagger}$	$\Delta H^{\ddagger}$	$\Delta G^{\ddagger}$	ν_i
2	-19.5	18.2	15.6	23.5	1475	-19.7	18.8	15.7	23.9	1501	-20.6	17.9	14.8	23.0	1491
3	-19.3	18.3	15.3	23.7	1486	-19.0	19.2	16.1	24.6	1520	-19.5	17.6	14.5	22.8	1480
4	-18.4	17.5	14.4	22.4	1461	-18.6	18.5	15.5	23.6	1490	-19.2	17.2	14.2	22.6	1480
5	-19.1	18.0	15.1	25.2	1504	-19.3	19.1	16.2	27.4	1531	-19.7	17.8	14.9	25.1	1524

Tunnelling calculations

We then carry out canonical variational theory[28-30] (CVT) calculations to determine the tunnelling contribution to the total reaction rate. The Page-McIver algorithm[31] (rpm *pagem*) is used to calculate the minimum energy path (MEP) from the saddle point towards the reactants and products. The first step is taken by following the direction defined by the normal mode of the imaginary frequency at the saddle point (firststep *nmode*). Energies and gradients are computed at every point along the MEP, and the Hessian is calculated every 9th step (inh *9*). We select a gradient step size of 0.002 bohr.amu$^{1/2}$ (sstep *0.002*), consistent with values used in recent literature.[28, 32-35] The method of central differences is used to compute the curvature along the MEP (curv *dgrad*). Generalized normal mode analyses performed at each Hessian grid point are carried out in redundant internal coordinates[28] (coord *curv3*). After the calculation of the MEP, the variational transition state is located as the point of maximum vibrationally-adiabatic energy[29] (Va^G). The effective reduced mass (μ_{eff}) is computed by spline interpolation[30] (sctopt *spline*). Finally, using the small curvature tunnelling[29, 36] (SCT) approximation, the transmission coefficient and tunnelling probabilities are computed. We select the widely used CVT/SCT method as it is relatively accurate while being computationally efficient.[28, 29]

The transmission coefficient, κ, which is the ratio of the total rate to the semiclassical rate (k_{SCT} / k_{CVT}), corrects for the effects of nonclassical reflection and tunnelling on the semiclassical rate. Since tunnelling takes place at lower energies than nonclassical reflection, the former is generally the dominant correction to the semiclassical rate. Thus, k_{SCT}, which corrects for both tunnelling and reflection, can be said to effectively correct for the former *alone;* and $\kappa = 1$ indicates no tunnelling, while $\kappa > 1$ indicates tunnelling. We calculate the percentage of the total rate due to tunnelling (%Tun) thus:

$$\%\text{Tun} = \frac{k_{SCT} - k_{CVT}}{k_{SCT}} = \frac{\kappa - 1}{\kappa} \qquad (1)$$

Calculating the entire MEP as required for CVT from *ab initio* electronic structure theory can be computationally demanding, potentially requiring several thousands of single-points, gradients, and Hessian calculations.[4, 30] Hence, we calculate the MEP to different extents (*s*) with and without extrapolation. Extrapolation is calculated using the Mapped Interpolation (MI) algorithm[37] with an extrapolation step size of 0.05 bohr.amu$^{1/2}$ (exstep *0.05*). Results in Table S3 below indicate that κ converges to about 13.9 when s = -1.5 to +1.5 bohr.amu$^{1/2}$ (slp *1.5* and slm *-1.5*) with and without extrapolation, indicating that tunnelling probabilities are already converged. Therefore, we report all results using s = -1.5 to +1.5 bohr.amu$^{1/2}$ in this work. The sample input files can be found in Section 3A of this document.

Table S3. Convergence of the SCT transmission coefficient (κ) with computed MEP extent (s) for chloride leaching from the two monomer-unit model at ωB97X-D(SMD=Water)/6-311+G(d,p) level of theory at 298 K. For each run, the MEP was computed from -s to +s (i.e. slm=-s and slp=s). Constant Polyrate 17 settings used were: coord=curv3, curv=dgrad, inh=9, norods, sstep=0.001 bohr, firststep=nmode, sctopt=spline, intmu=3, and rpm=pagem. For extrapolated MEPs, additional settings used were: exnstep=50 and exstep=0.05 bohr for both exfirst and exsecond.

s ($\mathbf{bohr.amu^{1/2}}$)	**Extrapolation**	κ
1.0	No	100.51
1.0	Yes	12.64
1.5	No	13.92
1.5	Yes	13.91
2.0	No	13.91
2.0	Yes	13.91
3.0	No	13.91
4.0	No	13.91
7.0	No	13.91

We also vary the above-mentioned parameters (sstep, rpm, sctopt, firststep, inh, curv, and coord) to observe the variation of κ to test the reliability of our settings. We present our results in Table S4 below. We observe a slight change in κ (from 13.91 to 13.69) when μ_{eff} is computed via Lagrangian interpolation (sctopt *lagrange*) rather than spline fitting. Furthermore, κ remains practically unchanged (13.91 vs. 13.92) when the starting algorithm is changed from a quadratic to a cubic one (firststep *cubic*). κ increases to 14.23 when the curvature along the MEP is computed using the Hessian, gradient, and normal-mode eigenvectors (curv *dhess*) rather than central differences. We observe a slight decrease in κ when the gradient step size is increased (κ = 13.91 and 9.56 for sstep = 0.002 and 0.004 respectively). This underestimation of κ by larger gradient step sizes has previously been noted by other researchers.[34] We also note a modest decrease (from 13.91 to 11.43) in κ when the method for following the MEP is changed from the Page-McIver integrator to Euler-steepest descents (rpm *esd*). Furthermore, κ barely changes to 12.86 when the Hessian is computed every 6th (rather than 9th) step along the MEP (inh *6*). The above discussion demonstrates that the tunnelling calculations for chloride leaching are very insensitive to the chosen parameters, as the tunnelling contribution (%Tun) only varies by 3% between 90% and 93% (Table S4). We conclude that our settings provide a reliable estimate on the tunnelling contribution to chloride leaching in PVC.

Table S4. Variation of the SCT transmission coefficient (κ), QT-corrected rate constant (k_{SCT}) in s^{-1}, and tunnelling contribution (%Tun) with respect to important settings in Polyrate 17 for chloride leaching from the two monomer-unit model at ωB97X-D(SMD=Water)/6-311+G(d,p) level at 298 K. Constant Polyrate-17 settings used: slp=1.5, slm=-1.5 (both in bohr.amu$^{1/2}$) – at these values, κ and k_{SCT} are already quite converged with respect to s – and extrapolation of the MEP (exnstep=50 and exstep=0.05 bohr.amu$^{1/2}$ for both exfirst and exsecond).

coord	curv	inh	rods	sstep	firststep	Sctopt	rpm	Results		
								κ	k_{SCT}	%Tun
curv3	dgrad	9	rods	0.002	nmode	Spline	pagem	14.85	1.4	93
curv3	dhess	9	norods	0.002	nmode	Spline	pagem	14.23	40.1	93
curv3	dgrad	9	norods	0.002	cubic	Spline	pagem	13.92	39.2	93
curv3	dgrad	9	norods	0.002	nmode	Spline	pagem	13.91	39.2	93
curv3	dgrad	9	norods	0.002	nmode	Spline	pagem	13.90	39.2	93
curv3	dgrad	9	norods	0.002	nmode	lagrange	pagem	13.69	38.5	93
cart	dgrad	9	norods	0.002	nmode	Spline	pagem	13.46	36.7	93
curv3	dgrad	6	norods	0.002	nmode	Spline	pagem	12.86	35.3	92
curv3	dgrad	9	norods	0.002	nmode	Spline	esd	11.43	32.2	91
curv3	dgrad	9	norods	0.004	nmode	Spline	pagem	9.56	26.9	90

2. Semiclassical and QT-corrected Rates

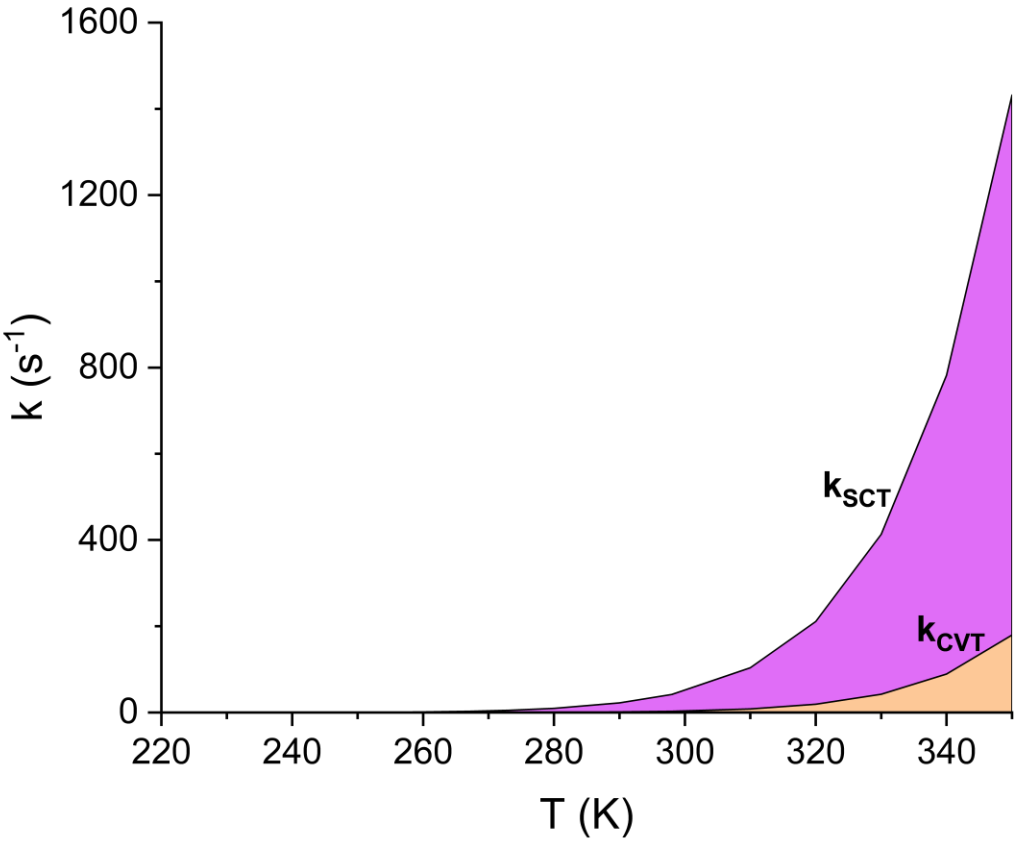

Figure S1. Plot of the QT-corrected rate constant (k_{SCT}) and semiclassical rate constant (k_{CVT}) versus temperature (in K) for chloride leaching from the two monomer-unit model at ωB97X-D(SMD=Water)/6-311+G(d,p) level of theory.

Table S5. Variation of the semiclassical rate constant (k_{CVT}) and QT-corrected rate constant (k_{SCT}) in s^{-1}, transmission coefficient (κ), and tunnelling contribution (%Tun) with respect to temperature (in K) for chloride leaching in the two monomer-unit model at ωB97X-D(SMD=Water)/6-311+G(d,p) level of theory. Low temperature results are only shown for the completeness of the calculated results; does not hold practical relevance.

T (K)	k_{CVT}	k_{SCT}	κ	%Tun
70	4.21×10^{-39}	1.89×10^{-16}	44.9×10^{21}	100
90	6.94×10^{-28}	9.29×10^{-15}	13.4×10^{12}	100
110	9.87×10^{-21}	2.71×10^{-12}	27.4×10^{7}	100
130	9.05×10^{-16}	6.77×10^{-10}	74.8×10^{4}	100
150	4.01×10^{-12}	8.45×10^{-8}	21.1×10^{3}	100
170	2.49×10^{-9}	5.46×10^{-6}	21.9×10^{2}	100
190	4.04×10^{-7}	1.93×10^{-4}	47.9×10^{1}	100
205	9.61×10^{-6}	1.98×10^{-3}	20.6×10^{1}	100
220	1.49×10^{-4}	1.57×10^{-2}	10.5×10^{1}	99
230	7.61×10^{-4}	5.51×10^{-2}	72.43	99
240	3.40×10^{-3}	1.77×10^{-1}	52.08	98
250	1.35×10^{-2}	5.24×10^{-1}	38.90	97
260	4.82×10^{-2}	1.45	30.00	97
267	1.11×10^{-1}	2.82	25.43	96
273	2.20×10^{-1}	4.89	22.28	96
280	4.70×10^{-1}	9.06	19.29	95
290	1.31	2.08×10^{1}	15.98	94
298	2.82	3.92×10^{1}	13.91	93
310	8.29	9.56×10^{1}	11.52	91
320	1.92×10^{1}	1.92×10^{2}	10.00	90
330	4.23×10^{1}	3.71×10^{2}	8.78	89
340	8.89×10^{1}	6.93×10^{2}	7.79	87
350	1.79×10^{2}	1.25×10^{3}	6.98	86

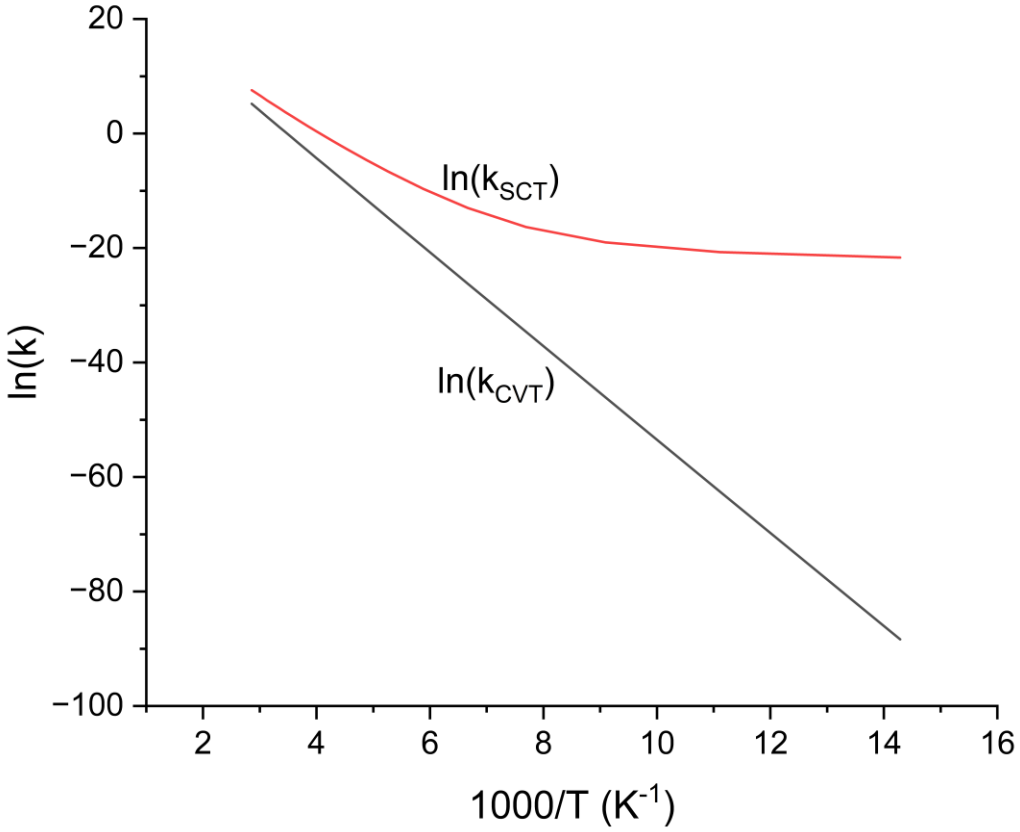

Figure S2. Arrhenius plot illustrating the shallow and deep tunnelling regimes for chloride leaching from the two monomer-unit model at ωB97X-D(SMD=Water)/6-311+G(d,p) level of theory. The temperature ranges from 70 – 350 K. Low temperature results are only shown for the completeness of the calculated results; does not hold practical relevance.

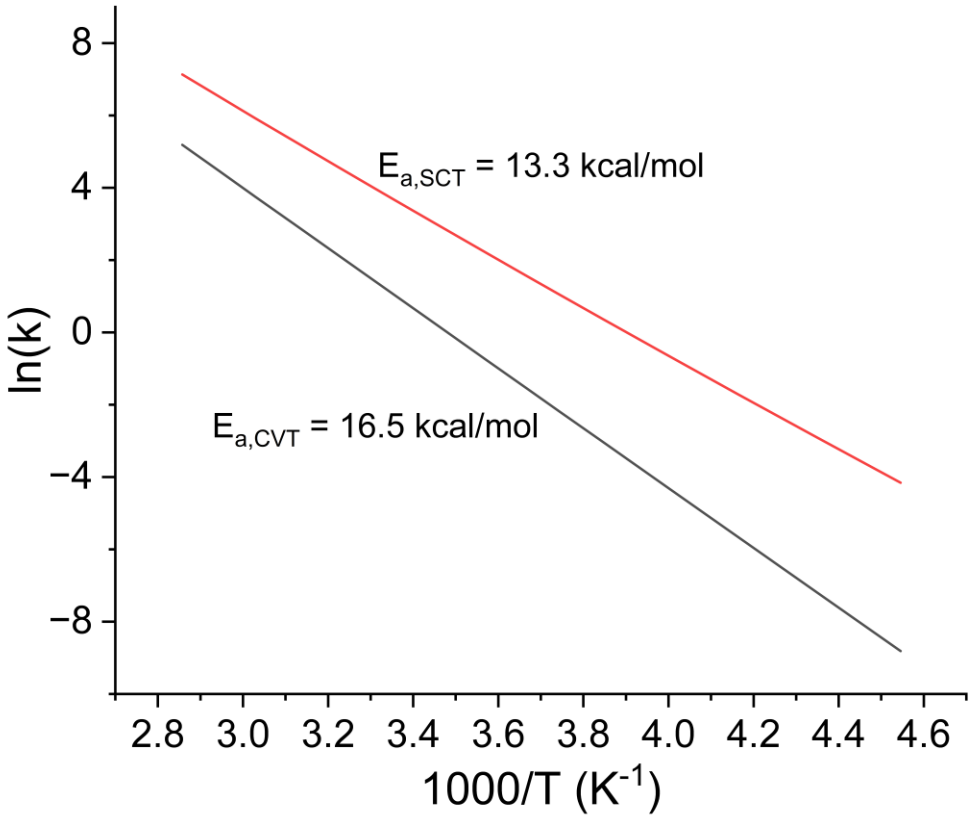

Figure S3. Arrhenius plots to get the semiclassical and tunnelling-corrected activation energies for chloride leaching from the two monomer-unit model for the temperature range of 220 – 350 K at ωB97X-D(SMD=Water)/6-311+G(d,p) level of theory.

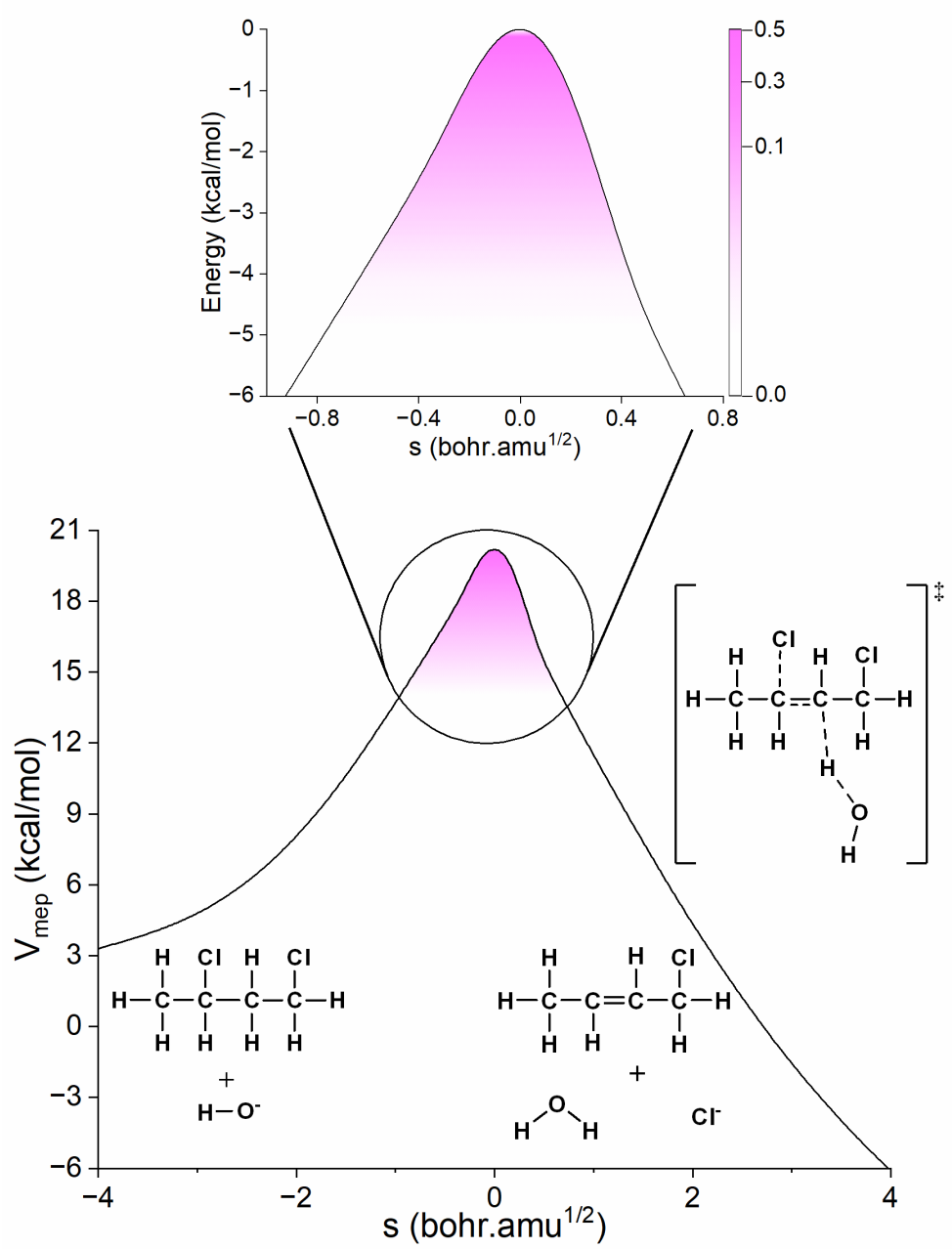

Figure S4. Potential energy curve of the minimum energy path (Vmep) as a function of the calculated mass-scaled reaction coordinate (s) at ωB97X-D(SMD=Water)/6-311+G(d,p) level of theory for the two monomer-unit model. The vertical axis of the inset is the potential energy relative to the transition state, and the vertical axis of the figure is the potential energy relative to the reactants. The shaded region is derived by plotting the tunnelling probabilities against s as derived from the Polyrate fu6 output file. 96 % of the tunnelling occurs within the shaded region. The values on the colour scale are the tunnelling probabilities.

3. Kinetic Isotope Effects (KIE) Analysis

We perform KIE analysis to discern the contribution of different atoms to the tunnelling phenomenon. We study the KIE in the leaving H, the C bonded to the leaving H, and the leaving Cl. In Table S6, we present our results between 70 and 350 K. The H/D KIE is 23.18 at 298 K, and ranges from 56.08 at 70 K to 16.44 at 350 K. Generally, a H/D KIE > 6 – 7 at room temperature indicates H-tunnelling,[27] hence the calculated H/D KIEs suggest that H-tunnelling is important in this reaction across the entire calculated temperature range (70 – 350 K). The C-12/C-14 KIE is 2.60 at 298 K and ranges from 5.73 to 2.46 at 70 K and 350 K respectively. The Cl-35/Cl-37 KIE is 2.51 at 298 K and ranges from 8.33 to 2.38 at 70 K and 350 K respectively. Though we note that a direct comparison of H/D KIEs with KIEs of other different elements is complicated by the difference in their masses, our results demonstrate that H-tunnelling is plays an important role in the overall QT.

Table S6. Calculated H/D, C-12/C-14, and Cl-35/Cl-37 KIEs between 70 K and 350 K for chloride leaching in the two monomer-unit model at the ωB97X-D(SMD=Water)/6-311+G(d,p) level of theory. Low temperature results are only shown for the completeness of the calculated results.

T(K)	KIE		
	H/D	C-12/C-14	Cl-35/Cl-37
70	56.08	5.73	8.33
90	54.35	3.29	3.99
110	75.99	3.70	3.79
130	88.09	4.12	3.93
150	76.85	3.98	3.72
170	63.67	3.66	3.44
190	53.70	3.37	3.18
205	47.63	3.18	3.02
220	42.35	3.03	2.89
230	39.10	2.95	2.83
240	36.20	2.88	2.76
250	33.41	2.82	2.70
260	30.94	2.76	2.65
267	29.32	2.73	2.61
273	27.97	2.70	2.59
280	26.56	2.67	2.57
290	24.64	2.63	2.53
298	23.18	2.60	2.51
310	21.33	2.56	2.48
320	19.93	2.53	2.45
330	18.65	2.51	2.43
340	17.50	2.48	2.41
350	16.44	2.46	2.38

4. Tunnelling Calculations with an Explicit Water Molecule Present

Implicit solvation models can be a source of error for reactive species such as OH^-. To test the validity of the implicit solvent model, we carry out electronic structure calculations and tunnelling calculations at the ωB97X-D(SMD=Water)/6-311+G(d,p) level of theory on a two monomer-unit model with an explicit water molecule present. On including the explicit water molecule into the calculations, we still assume that all reactants are infinitely separated from each other, and the water has a concentration of 55.56 mol/l corresponding to the concentration of liquid water. With such reference state, ΔG_R increases by 5.2 kcal/mol to -25.7 kcal/mol, while ΔE_R decreases by 3.3 kcal/mol to -23.9 kcal/mol. On the other hand, $\Delta G^{\ddagger}$ decreases by 11 kcal/mol to 22.2 kcal/mol, and $\Delta E^{\ddagger}$ decreases by 7 kcal/mol to 10.9 kcal/mol.

Table S7. Variation of the semiclassical rate constant (k_{CVT}) and QT-corrected rate constant (k_{SCT}) in s^{-1}, transmission coefficient (κ), and tunnelling contribution (%Tun) with respect to temperature (in K) for chloride leaching in the two monomer-unit model at ωB97X-D(SMD=Water)/6-311+G(d,p) level of theory, with an explicit water molecule present.

T (K)	k_{CVT}	k_{SCT}	κ	%Tun
70	5.93×10^{-44}	1.81×10^{-19}	3.06×10^{24}	100
90	1.20×10^{-31}	6.91×10^{-18}	5.75×10^{13}	100
110	8.34×10^{-24}	2.15×10^{-15}	2.58×10^{8}	100
130	2.28×10^{-18}	8.59×10^{-13}	3.78×10^{5}	100
150	2.24×10^{-14}	1.76×10^{-10}	7.89×10^{3}	100
170	2.56×10^{-11}	1.91×10^{-8}	7.46×10^{2}	100
190	6.70×10^{-9}	1.10×10^{-6}	1.64×10^{2}	99
205	2.15×10^{-7}	1.58×10^{-5}	73.28	99
220	4.33×10^{-6}	1.71×10^{-4}	39.41	97
230	2.58×10^{-5}	7.26×10^{-4}	28.11	96
240	1.33×10^{-4}	2.79×10^{-3}	21.01	95
250	6.01×10^{-4}	9.81×10^{-3}	16.32	94
260	2.42×10^{-3}	3.17×10^{-2}	13.08	92
267	6.05×10^{-3}	6.89×10^{-2}	11.39	91
273	1.28×10^{-2}	1.30×10^{-1}	10.21	90
280	2.94×10^{-2}	2.66×10^{-1}	9.07	89
290	9.00×10^{-2}	7.00×10^{-1}	7.78	87
298	2.09×10^{-1}	1.45	6.96	86

310	6.83×10^{-1}	4.09	5.99	83
320	1.71	9.19	5.36	81
330	4.07	19.72	4.84	79
340	9.21	40.66	4.42	77
350	19.9	80.71	4.06	75

5. Sample Polyrate Input and Output Files

A. Sample Polyrate Input Files

We list Polyrate and Gaussrate input files for the tunnelling calculations on the two monomer-unit model at the ωB97X-D(SMD=Water)/6-311+G(d,p) level of theory. Gaussrate was used for interfacing Polyrate to Gaussian for electronic structure calculations.

tunnel.dat

```
*General
 TITLE
  C4H8Cl2 + OH- ---> C4H7Cl + Cl- + H2O
  CVT/SCT calculations
 END

 ATOMS
  1  C
  2  C
  3  C
  4  C
  5  CL
  6  CL
  7  O
  8  H
  9  H
 10  H
 11  H
 12  H
 13  H
 14  H
 15  H
 16  H
 END

 NOSUPERMOL
 INPUNIT au

*OPTIMIZATION
 OPTMIN   ohook
```

```
 OPTTS    ohook

*SECOND
 HESSCAL hhook

*REACT1
#  STATUS 2
 INITGEO HOOKS
 GEOM
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
 END
 SPECIES  NONLINRP

*PROD1
#  STATUS  2
 INITGEO HOOKS
 GEOM
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
 END
 SPECIES   NONLINRP

*START
 STATUS 2
 GEOM
  1 0.048046306 -0.677249767 -2.175529171
  2 -0.005637055 -0.729323081 0.658898629
```

```
 3 2.430562931 -0.69888336 1.836134224
 4 2.533965006 -0.879280468 4.665546689
 5 -3.028245748 0.189399766 -3.51159253
 6 4.640607963 -3.926442381 0.686834462
 7 -1.881842937 3.606044858 2.247438948
 8 3.760766246 0.647091616 1.035022308
 9 -1.261938822 -2.188005148 1.411601411
10 1.413997585 -2.468329122 5.35771018
11 4.465980192 -1.050516179 5.357143262
12 1.72663211 0.864797601 5.43824656
13 1.37438513 0.725840314 -2.893810578
14 0.465866808 -2.506227595 -3.027797882
15 -0.932302424 1.509408005 1.509383439
16 -1.190155657 3.82148695 3.91289304
END
SPECIES  NONLINTS
PROJECT

*RATE
 FORWARDK
 SIGMAF     1
 CVT
 TST
 TEMP
220
250
273
298
300
320
350
 END
 EACT
  273  298
 END
ANALYSIS
  273  298
END

*TUNNEL
 ZCT
 SCT
 WIGNER
 SCTOPT
  SPLINE
 END

*PATH
 INTMU   3
 INH    9
 SSTEP  0.002
 SRANGE
  SLP  7
  SLM  -7
 END
 RPM   pagem
```

```
 COORD  curv3                                  2-9 1-2-9 5-1-2-9
 CURV   dgrad                                  4-10 3-4-10 2-3-4-10
 SIGN  product                                 4-11 3-4-11 2-3-4-11
 SADDLE                                        4-12 3-4-12 2-3-4-12
 INTDEF                                        1-13 2-1-13 3-2-1-13
  1-5 1-2 5-1-2                                1-14 2-1-14 3-2-1-14
  2-3 1-2-3 5-1-2-3                            7-15 2-7-15 1-2-7-15
  3-4 2-3-4 1-2-3-4                            7-16 2-7-16 1-2-7-16
  3-6 2-3-6 1-2-3-6                           END
  2-7 1-2-7 5-1-2-7
  3-8 2-3-8 1-2-3-8                           #end of file
```

tunnel.70

```
*GRGENERAL
 GRRESTART
*GRREACT1
  charge -1
  multiplicity 1
*GRPROD1
  charge -1
  multiplicity 1
*GRSTART
  charge -1
  multiplicity 1
*GRCOMMON
 GRENER
  %mem=85gb
  %nprocshared=28
```

#wB97XD/6-311+G(d,p) UNITS=AU FCHK NOSYMM SCRF = (SMD) int=UltraFine

END

GRFIRST

%mem=85gb

%nprocshared=28

#wB97XD/6-311+G(d,p) FORCE UNITS=AU FCHK NOSYMM SCRF = (SMD) int=UltraFine

END

GRSEC

%mem=85gb

%nprocshared=28

#wB97XD/6-311+G(d,p) FREQ=NORAMAN UNITS=AU FCHK NOSYMM SCRF = (SMD) int=UltraFine

END

*GRPATH

GRENER

%chk = guess.chk

%mem=85gb

%nprocshared=28

#wB97XD/6-311+G(d,p) UNITS=AU FCHK NOSYMM SCRF = (SMD) int=UltraFine

END

GRFIRST

%chk = guess.chk

%mem=85gb

%nprocshared=28

#wB97XD/6-311+G(d,p) FORCE UNITS=AU FCHK NOSYMM SCRF = (SMD) int=UltraFine

END

GRSEC

%chk = guess.chk

%mem=85gb

%nprocshared=28

#wB97XD/6-311+G(d,p) FREQ=NORAMAN UNITS=AU FCHK NOSYMM SCRF = (SMD) int=UltraFine

END

#end of keywords

tunnel.71

#wB97XD 6-311+G(d,p) opt=calcfc int(ultrafine) nosymm fchk SCRF=(SMD, SOLVENT=Water)

react1

-1 1

C	-0.075992	-0.281413	-1.012614
C	-0.039549	-0.732601	0.433383
C	1.324820	-0.542506	1.077101
C	1.317763	-0.847064	2.559212
Cl	-1.767347	-0.355359	-1.663959
Cl	2.564110	-1.623016	0.249846
O	-0.492427	2.967583	0.725991
H	1.697191	0.465324	0.891162
H	-0.351194	-1.777194	0.522558
H	0.974826	-1.867419	2.748265
H	2.309759	-0.717451	2.994820
H	0.631604	-0.153349	3.053577
H	0.240687	0.755459	-1.116758
H	0.519956	-0.916704	-1.663987
H	-0.739621	-0.124870	1.016213

H	0.012771	2.159184	0.836868

tunnel.73

#wB97XD 6-311+G(d,p) opt=calcfc int(ultrafine) nosymm fchk SCRF=(SMD, SOLVENT=Water)

prod1

-1 1

C	-0.102025	-0.094621	-0.012024
C	-0.051015	-0.036763	1.471353
C	1.092575	0.043875	2.151441
C	1.203583	0.067726	3.640231
Cl	-0.907845	1.402665	-0.702126
Cl	3.211214	3.511935	3.242478
O	0.154136	3.268638	2.600066
H	2.027085	0.096437	1.593647
H	-1.001995	-0.087473	1.998359
H	0.222245	0.037426	4.119157
H	1.792748	-0.784781	3.993542
H	1.728768	0.972933	3.963099
H	0.889094	-0.130529	-0.459191
H	-0.708021	-0.922500	-0.375054
H	0.033465	2.377174	2.255454

H 1.109780 3.316346 2.804812

B. Sample Polyrate Output Files

tunnel.fu15

Summary of forward rate constants in s^{-1}

T(K)	TST	CVT	CVT/ZCT	CVT/SCT
220.00	1.49E-04	1.49E-04	2.66E-03	1.57E-02
250.00	1.35E-02	1.35E-02	1.29E-01	5.24E-01
273.00	2.20E-01	2.20E-01	1.48E+00	4.89E+00
298.00	2.82E+00	2.82E+00	1.41E+01	3.92E+01
300.00	3.39E+00	3.39E+00	1.67E+01	4.57E+01
320.00	1.92E+01	1.92E+01	7.83E+01	1.92E+02
350.00	1.79E+02	1.79E+02	5.84E+02	1.25E+03

Parts of tunnel.fu6

Vibrationally adiabatic ground-state transmission coefficients

$kappa^{+/CAG}$ - the classical transmission coefficient for correcting the classical threshold of conventional TST

$kappa^{ZCT}$ - semiclassical transmission coefficient for tunnelling along MEP with zero curvature

$kappa^{SCT}$ - semiclassical transmission coefficient for tunnelling along MCP, in small curvature limit.

Kappa factors

T(K)	TST/W	TST/CAG	CVT/CAG
220	4.93E+00	9.99E-01	9.99E-01
250	4.05E+00	9.99E-01	9.99E-01
273	3.56E+00	9.99E-01	9.99E-01
298	3.14E+00	9.99E-01	9.99E-01
300	3.12E+00	9.99E-01	9.99E-01
320	2.86E+00	9.99E-01	9.99E-01
350	2.55E+00	9.99E-01	9.99E-01

T(K)	ZCT	SCT
220	1.79E+01	1.05E+02
250	9.57E+01	3.89E+02
273	6.74E+01	2.23E+01
298	5.02E+00	1.39E+01
300	4.91E+00	1.35E+01
320	4.08E+00	9.99E+00
350	3.26E+00	6.98E+00

6. Cartesian Coordinates of Stationary Points

A. Cartesian Coordinates of Stationary Points Used in Polyrate

Presented below are the cartesian coordinates of the reactant (*react1*), product (*prod1*), and transition state (*start*) used for the tunnelling calculations on the two monomer-unit model at the ωB97X-D(SMD=Water)/6-311+G(d,p) level of theory

The Reactant is an ion complex of the reactant molecules (OH^- and the two monomer-unit model PVC), which proceeds to the Transition State. The Product is a complex of the dehydrochlorinated reactant, H_2O, and Cl^-

REACTANT

C	-0.075992	-0.281413	-1.012614
C	-0.039549	-0.732601	0.433383
C	1.324820	-0.542506	1.077101
C	1.317763	-0.847064	2.559212
Cl	-1.767347	-0.355359	-1.663959
Cl	2.564110	-1.623016	0.249846
O	-0.492427	2.967583	0.725991
H	1.697191	0.465324	0.891162
H	-0.351194	-1.777194	0.522558
H	0.974826	-1.867419	2.748265
H	2.309759	-0.717451	2.994820
H	0.631604	-0.153349	3.053577
H	0.240687	0.755459	-1.116758
H	0.519956	-0.916704	-1.663987
H	-0.739621	-0.124870	1.016213
H	0.012771	2.159184	0.836868

TRANSITION STATE

C	0.025425	-0.358385	-1.151240
C	-0.002983	-0.385941	0.348674
C	1.286198	-0.369833	0.971640
C	1.340916	-0.465295	2.468900
Cl	-1.602478	0.100226	-1.858254
Cl	2.455703	-2.077783	0.363457
O	-0.995828	1.908236	1.189293
H	1.990111	0.342426	0.547710
H	-0.667789	-1.157842	0.746987
H	0.748255	-1.306183	2.835177

H	2.363294	-0.555909	2.834877
H	0.913694	0.457631	2.877795
H	0.727293	0.384098	-1.531338
H	0.246526	-1.326238	-1.602241
H	-0.493353	0.798744	0.798731
H	-0.629803	2.022243	2.070613

PRODUCT

C	-0.102025	-0.094621	-0.012024
C	-0.051015	-0.036763	1.471353
C	1.092575	0.043875	2.151441
C	1.203583	0.067726	3.640231
Cl	-0.907845	1.402665	-0.702126
Cl	3.211214	3.511935	3.242478
O	0.154136	3.268638	2.600066
H	2.027085	0.096437	1.593647
H	-1.001995	-0.087473	1.998359
H	0.222245	0.037426	4.119157
H	1.792748	-0.784781	3.993542
H	1.728768	0.972933	3.963099
H	0.889094	-0.130529	-0.459191
H	-0.708021	-0.922500	-0.375054
H	0.033465	2.377174	2.255454
H	1.109780	3.316346	2.804812

Presented below are the cartesian coordinates of the reactant (*react1*), product (*prod1*), and transition state (*start*) used for the tunnelling calculations on the two monomer-unit model including an explicit water molecule at the ωB97X-D(SMD=Water)/6-311+G(d,p) level of theory

The Reactant is a complex of the reactant molecules (OH^-, H2O, and the two monomer-unit model PVC), which proceeds to the Transition State. The Product is a complex of the dehydrochlorinated reactant, two H_2O molecules, and Cl^-

REACTANT

C	0.061774	0.176290	-0.000960
Cl	0.165390	-0.245610	1.761657
C	1.422316	0.065794	-0.657849
C	1.401065	0.456091	-2.127292
C	2.788133	0.546853	-2.724733
Cl	0.414203	-0.768313	-3.084091
O	2.481901	2.566760	1.901230
O	1.655528	3.642951	-0.295881
H	2.116175	0.752645	-0.162832
H	2.000134	1.746286	2.030308
H	1.963793	3.186291	0.561515
H	0.990732	3.056515	-0.664239
H	-0.327095	1.192812	-0.044264
H	-0.665336	-0.513317	-0.424323
H	1.822642	-0.946392	-0.551695
H	0.857013	1.389429	-2.272116
H	3.328012	-0.396116	-2.606984
H	2.746948	0.805002	-3.784100
H	3.341309	1.331170	-2.200067

PRODUCT

C	0.016458	-0.115576	-0.085023
C	0.048595	-0.312155	1.387182
C	1.046376	0.130487	2.151365
C	1.158289	-0.086509	3.624863
Cl	-1.448247	0.863784	-0.591464
Cl	4.165802	-2.468112	1.376058
O	-0.955588	2.796881	2.501661
O	1.116671	3.457988	0.678947
H	1.854451	0.689708	1.681352
H	-0.771803	-0.877364	1.825262
H	0.304621	-0.643565	4.017383
H	2.074437	-0.637764	3.860032
H	1.223508	0.872672	4.148631
H	0.885063	0.429505	-0.450227
H	-0.086637	-1.055788	-0.624204
H	-0.754724	1.853559	2.534419
H	-1.770959	2.848174	1.993323
H	0.398792	3.243296	1.300609
H	1.423888	2.602510	0.366917

TRANSITION STATE

C	0.000735	0.000757	0.001557
Cl	0.004103	-0.018698	1.833246
C	1.391390	-0.000744	-0.561837
C	1.512095	0.488593	-1.890669
C	2.852204	0.455061	-2.554900
Cl	0.298731	-0.789837	-3.279059
O	2.761277	1.836148	0.745160
O	0.977586	3.621757	-0.170755
H	0.906300	1.358090	-2.129783
H	1.935466	-0.930098	-0.376426

H	3.329909	-0.520227	-2.444476
H	2.789472	0.715365	-3.610641
H	3.481794	1.202543	-2.057619
H	-0.552339	0.896842	-0.279518
H	-0.575368	-0.881323	-0.276399
H	2.101435	0.931558	0.071879
H	2.533934	1.654434	1.661437
H	1.646031	2.982705	0.188105
H	0.330069	3.065031	-0.611116

B. Cartesian Coordinates of All Structures

We present the cartesian coordinates of optimized stationary points in the basis set and functional benchmarking. The Reactant in each section is a PVC model, which reacts with the hydroxide ion, forming the studied E2 Transition State. From the Transition State, H_2O, and Cl^-, and the Product are formed.

Model: 2 monomer units

Level of theory: ωB97X-D(SMD=Water)/6-31+G(d,p)

Reactant

0 1

C	-0.013515	-0.007895	-0.008429
C	-0.019678	0.012715	1.507536
Cl	1.717084	-0.027622	2.112003
C	-0.739534	1.230866	2.072149
C	-0.864225	1.196866	3.584202
Cl	-1.856680	2.595380	4.177436
H	0.452733	0.896026	-0.411624
H	-1.048663	-0.052186	-0.362117
H	0.517317	-0.883200	-0.389687
H	-0.455960	-0.906255	1.903967

H	-1.740952	1.229491	1.627318
H	-0.232387	2.145582	1.747600
H	-1.373955	0.295457	3.926415
H	0.100195	1.283969	4.083354

OH-

-1 1

O	0.000000	0.000000	-0.007799
H	0.000000	0.000000	0.954799

Transition State

-1 1

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.502978
C	1.305100	0.000000	2.099591
C	1.388253	-0.074431	3.599121
Cl	-1.632655	0.470871	-0.687074
Cl	2.430798	-1.738649	1.493990
O	-0.944783	2.320212	2.324319
H	2.012804	0.696180	1.651816
H	-0.669275	-0.757197	1.925714
H	0.787070	-0.899454	3.990241
H	2.417187	-0.180078	3.945932
H	0.986907	0.863328	4.003019
H	0.708951	0.724184	-0.406228
H	0.201014	-0.980913	-0.436063
H	-0.465645	1.201732	1.943586
H	-0.558954	2.450619	3.198467

Product

0 1

C 0.000000 0.000000 0.000000

C 0.000000 0.000000 1.490952

C 1.087903 0.000000 2.251380

C 1.035954 0.033177 3.732546

Cl 1.695180 -1.517859 4.445647

H -0.526768 0.875546 -0.385350

H 1.012594 -0.001290 -0.402408

H -0.528018 -0.876343 -0.382286

H -0.972706 0.004381 1.975432

H 2.073923 -0.008500 1.797946

H 1.661616 0.813965 4.154811

H 0.021976 0.124237 4.108997

H2O

0 1

O 0.009066 0.000000 0.007019

H 0.007974 -0.000000 0.970592

H 0.941632 0.000000 -0.235461

Cl-

-1 1

Cl 0.000000 0.000000 0.000000

Model: 2 monomer units

Level of theory: ωB97X-D(SMD=Water)/6-31++G(d,p)

Reactant

0 1

C	-0.013515	-0.007895	-0.008429
C	-0.019678	0.012715	1.507536
Cl	1.717084	-0.027622	2.112003
C	-0.739534	1.230866	2.072149
C	-0.864225	1.196866	3.584202
Cl	-1.856680	2.595380	4.177436
H	0.452733	0.896026	-0.411624
H	-1.048663	-0.052186	-0.362117
H	0.517317	-0.883200	-0.389687
H	-0.455960	-0.906255	1.903967
H	-1.740952	1.229491	1.627318
H	-0.232387	2.145582	1.747600
H	-1.373955	0.295457	3.926415
H	0.100195	1.283969	4.083354

OH-

-1 1

O	0.000000	0.000000	-0.007799
H	0.000000	0.000000	0.954799

Transition State

-1 1

C	-0.331891	0.046837	-1.209415
C	-0.360937	0.022348	0.293032
C	0.932464	0.033970	0.914606

C	0.988171	-0.061847	2.414190
Cl	-1.958034	0.503832	-1.920991
Cl	2.096946	-1.676494	0.304918
O	-1.358082	2.314106	1.132119
H	1.636789	0.748545	0.491113
H	-1.025298	-0.752625	0.690513
H	0.393188	-0.902292	2.781284
H	2.011917	-0.156361	2.779091
H	0.564027	0.863153	2.824162
H	0.373371	0.788349	-1.589982
H	-0.107246	-0.923696	-1.657041
H	-0.854531	1.209593	0.743811
H	-0.995322	2.434089	2.017548

Product

0 1

C	-0.003225	0.000833	-0.007194
C	-0.003189	-0.003238	1.488756
C	1.093087	-0.000474	2.252791
C	1.039775	0.032777	3.738885
Cl	1.690582	-1.524611	4.461264
H	-0.533211	0.879830	-0.390965
H	1.013163	0.002779	-0.411070
H	-0.530517	-0.879401	-0.392322
H	-0.979346	-0.003776	1.975568
H	2.082381	-0.003658	1.796541
H	1.670793	0.814969	4.161116
H	0.021362	0.131284	4.114297

H2O

0 1

O 0.009066 0.000000 0.007019

H 0.007974 -0.000000 0.970592

H 0.941632 -0.000000 -0.235461

Cl-

-1 1

Cl 0.000000 0.000000 0.000000

Model: 2 monomer units

Level of theory: ωB97X-D(SMD=Water)/6-311+G(d,p)

Reactant

0 1

C -0.016447 -0.009191 -0.006117

C -0.018417 0.015613 1.507161

Cl 1.721489 -0.018962 2.105414

C -0.736319 1.231360 2.072540

C -0.866535 1.193073 3.581797

Cl -1.853687 2.594850 4.174923

H 0.446366 0.893764 -0.412225

H -1.051377 -0.055587 -0.356900

H 0.513997 -0.883528 -0.386549

H -0.447079 -0.902398 1.909060

H -1.734898 1.234826 1.624389

H	-0.225999	2.144274	1.752327
H	-1.383432	0.296009	3.919106
H	0.094117	1.275090	4.085198

OH-

-1 1

O	0.000000	0.000000	-0.006234
H	0.000000	0.000000	0.953234

Transition State

-1 1

C	0.025425	-0.358385	-1.151240
C	-0.002983	-0.385941	0.348674
C	1.286198	-0.369833	0.971640
C	1.340916	-0.465295	2.468900
Cl	-1.602478	0.100226	-1.858254
Cl	2.455703	-2.077783	0.363457
O	-0.995828	1.908236	1.189293
H	1.990111	0.342426	0.547710
H	-0.667789	-1.157842	0.746987
H	0.748255	-1.306183	2.835177
H	2.363294	-0.555909	2.834877
H	0.913694	0.457631	2.877795
H	0.727293	0.384098	-1.531338
H	0.246526	-1.326238	-1.602241
H	-0.493353	0.798744	0.798731
H	-0.629803	2.022243	2.070613

Product

0 1

C	-0.001616	-0.000463	-0.003565
C	-0.000759	-0.003204	1.490086
C	1.091712	0.002280	2.251648
C	1.037866	0.035265	3.735195
Cl	1.682978	-1.527087	4.451996
H	-0.533825	0.875952	-0.386944
H	1.013271	0.003485	-0.407584
H	-0.527367	-0.880888	-0.387107
H	-0.975477	-0.005211	1.977112
H	2.080172	0.001247	1.796545
H	1.672845	0.810987	4.158988
H	0.021853	0.134952	4.111297

H2O

0 1

O	0.009010	0.000000	0.006975
H	0.010130	-0.000000	0.967865
H	0.939532	0.000000	-0.232691

Cl-

-1 1

Cl	0.000000	0.000000	0.000000

Model: 2 monomer units

Level of theory: ωB97X-D(SMD=Water)/6-311++G(d,p)

Reactant

0 1

C	-0.017301	-0.009838	-0.005992
C	-0.017372	0.016232	1.507288
Cl	1.723546	-0.015141	2.103134
C	-0.735456	1.231915	2.072435
C	-0.868060	1.192024	3.581407
Cl	-1.850236	2.597272	4.174607
H	0.442062	0.894368	-0.413196
H	-1.052549	-0.059886	-0.355330
H	0.515553	-0.882827	-0.386139
H	-0.443987	-0.902044	1.910720
H	-1.733581	1.236702	1.623236
H	-0.223636	2.144651	1.754342
H	-1.389278	0.296782	3.916925
H	0.092074	1.268983	4.086688

OH-

-1 1

O	0.000000	0.000000	-0.006234
H	0.000000	0.000000	0.953234

Transition State

-1 1

C	0.025253	-0.358047	-1.150849

C	-0.003397	-0.386158	0.349039
C	1.285778	-0.369690	0.971854
C	1.340602	-0.465719	2.469075
Cl	-1.603562	0.096662	-1.858025
Cl	2.455971	-2.077117	0.363294
O	-0.993808	1.909724	1.187977
H	1.989442	0.342817	0.547926
H	-0.668265	-1.157971	0.747272
H	0.747279	-1.306332	2.834904
H	2.363018	-0.557373	2.834633
H	0.914187	0.457309	2.878570
H	0.725325	0.386242	-1.530779
H	0.249006	-1.325173	-1.602225
H	-0.493081	0.799236	0.798221
H	-0.628567	2.021784	2.069894

Product

0 1

C	-0.001616	-0.000463	-0.003565
C	-0.000759	-0.003204	1.490086
C	1.091712	0.002280	2.251648
C	1.037866	0.035265	3.735195
Cl	1.682978	-1.527087	4.451996
H	-0.533825	0.875952	-0.386944
H	1.013271	0.003485	-0.407584
H	-0.527367	-0.880888	-0.387107
H	-0.975477	-0.005211	1.977112
H	2.080172	0.001247	1.796545

H 1.672845 0.810987 4.158988

H 0.021853 0.134952 4.111297

H2O

0 1

O 0.009010 0.000000 0.006975

H 0.010130 -0.000000 0.967865

H 0.939532 0.000000 -0.232691

Cl-

-1 1

Cl 0.000000 0.000000 0.000000

Model: 2 monomer units

Level of theory: ωB97X-D(SMD=Water)/aug-cc-pVTZ

Reacant

0 1

C -2.170215 1.505460 -0.097031

C -1.214367 0.434888 0.374199

H -2.201548 1.548121 -1.185830

H -3.175667 1.329298 0.280320

H -1.826523 2.471094 0.276864

H -1.212874 0.368581 1.459292

Cl -1.847215 -1.202453 -0.159563

C 0.196358 0.639557 -0.148016

C 1.186570 -0.350996 0.421758

H	0.195798	0.597154	-1.238041
H	0.490082	1.649825	0.143629
Cl	2.865754	0.033642	-0.132156
H	1.212620	-0.315773	1.507111
H	0.993438	-1.367033	0.093888

OH-

-1 1

O	0.000000	0.000000	0.105693
H	0.000000	0.000000	-0.852970

Transition State

-1 1

C	0.126652	0.266986	-0.311947
C	-1.194233	0.392619	0.221695
C	0.995129	-0.735386	0.379649
H	-1.241899	0.434420	1.304421
C	-2.132104	1.341260	-0.463588
H	0.149033	0.170032	-1.398246
H	-3.135925	1.288724	-0.049980
H	-1.753947	2.355623	-0.313535
H	-2.173856	1.149804	-1.535190
Cl	2.779055	-0.417239	0.091543
H	0.872107	-0.702632	1.459422
H	0.856344	-1.756950	0.033725
Cl	-2.251888	-1.453093	0.110783
H	0.623630	1.509542	-0.037916
O	1.138748	2.641999	0.201169

H 2.074312 2.436671 0.267364

Product

0 1

C 0.257197 -3.012345 0.000000

H 1.077823 -3.727488 0.000000

H -0.357943 -3.211057 0.879180

C 0.770575 -1.600087 0.000000

H -0.357943 -3.211057 -0.879180

C -0.002610 -0.523779 0.000000

H 1.848717 -1.466730 0.000000

C 0.553103 0.871035 0.000000

H -1.082885 -0.626436 0.000000

Cl -0.762618 2.110146 0.000000

H 1.150934 1.075986 0.883977

H 1.150934 1.075986 -0.883977

H2O

0 1

H 0.000000 0.758695 -0.467425

O 0.000000 -0.000000 0.120719

H -0.000000 -0.758695 -0.467425

Cl-

-1 1

Cl 0.000000 0.000000 0.000000

Model: 2 monomer units

Level of theory: ωB97X-D(SMD=Water)/def2-TZVPPD

Reactant

0 1

C	-2.170203	1.504232	-0.097590
C	-1.214694	0.432154	0.373150
H	-2.203309	1.546801	-1.186691
H	-3.175956	1.329858	0.281245
H	-1.825110	2.469975	0.275620
H	-1.211853	0.370818	1.459245
Cl	-1.845125	-1.199990	-0.155595
C	0.196733	0.639881	-0.148342
C	1.188606	-0.350513	0.419942
H	0.197102	0.600069	-1.238874
H	0.489127	1.650206	0.145666
Cl	2.863138	0.032464	-0.129395
H	1.210539	-0.317781	1.506197
H	0.993216	-1.366808	0.091847

OH-

-1 1

O	0.000000	0.000000	0.105139
H	0.000000	0.000000	-0.852416

Transition State

-1 1

C	0.126803	0.267311	-0.311663

C	-1.197099	0.386152	0.221264
C	0.996892	-0.735480	0.378632
H	-1.242374	0.434629	1.304470
C	-2.133051	1.339281	-0.462874
H	0.148683	0.168737	-1.398381
H	-3.138336	1.287067	-0.051533
H	-1.754716	2.353346	-0.310025
H	-2.173968	1.150836	-1.535437
Cl	2.775230	-0.423248	0.086959
H	0.874356	-0.701433	1.459117
H	0.853262	-1.758537	0.036631
Cl	-2.245477	-1.445631	0.109076
H	0.628557	1.518232	-0.035918
O	1.138338	2.640823	0.202811
H	2.074060	2.440297	0.266238

Product

0 1

C	-0.000309	-0.000001	-0.000775
C	-0.000248	0.000200	1.490273
C	1.088053	0.000099	2.251069
C	1.036754	0.033076	3.733076
Cl	1.698679	-1.509004	4.446325
H	-0.526646	0.876141	-0.386167
H	1.012465	-0.002077	-0.403530
H	-0.529216	-0.876220	-0.382912
H	-0.973371	0.004605	1.974879
H	2.074445	-0.007936	1.797234

H 1.658668 0.819088 4.152809

H 0.021774 0.123810 4.108522

H2O

0 1

H 0.000000 0.758384 -0.466808

O -0.000000 0.000000 0.119487

H -0.000000 -0.758384 -0.466808

Cl-

-1 1

Cl 0.000000 0.000000 0.000000

Model: 2 monomer units

Level of theory: ωB97X-D(SMD=Water)/def2-QZVPPD

Reactant

0 1

C -2.169628 1.504353 -0.097118

C -1.214945 0.431321 0.372523

H -2.202634 1.547902 -1.185359

H -3.174703 1.330159 0.281132

H -1.824366 2.468800 0.276740

H -1.212307 0.369068 1.457742

Cl -1.845530 -1.198832 -0.157549

C 0.196313 0.639369 -0.148544

C 1.188623 -0.349793 0.420549

H	0.196981	0.598571	-1.238264
H	0.488044	1.649284	0.144480
Cl	2.861733	0.032317	-0.130306
H	1.211359	-0.315260	1.505870
H	0.993269	-1.365891	0.094527

OH-

-1 1

O	0.000000	0.000000	0.104901
H	0.000000	0.000000	-0.852178

Transition State

-1 1

C	0.126403	0.266948	-0.312133
C	-1.197074	0.385601	0.220802
C	0.996891	-0.734956	0.378260
H	-1.241769	0.435318	1.303246
C	-2.132444	1.338991	-0.463542
H	0.148073	0.167639	-1.398093
H	-3.136913	1.287605	-0.052240
H	-1.753851	2.352180	-0.311701
H	-2.173918	1.149829	-1.535159
Cl	2.774110	-0.422847	0.085690
H	0.874997	-0.700158	1.458009
H	0.853565	-1.757644	0.037479
Cl	-2.244931	-1.443787	0.110274
H	0.628229	1.518959	-0.035417
O	1.137423	2.640137	0.205196

H 2.072370 2.438566 0.268698

Product

0 1

C 0.001056 -0.002208 0.001983

C 0.003374 -0.009372 1.492641

C 1.092236 0.003156 2.250950

C 1.042688 0.028503 3.732793

Cl 1.727954 -1.506346 4.437390

H -0.538544 0.867182 -0.377870

H 1.012329 0.012869 -0.401990

H -0.514859 -0.883701 -0.383297

H -0.968204 -0.021868 1.978468

H 2.077229 0.012141 1.795923

H 1.653281 0.820780 4.155032

H 0.027895 0.102364 4.109959

H2O

0 1

H 0.000000 0.757767 -0.466831

O -0.000000 -0.000000 0.119531

H -0.000000 -0.757767 -0.466831

Cl-

-1 1

Cl 0.000000 0.000000 0.000000

Model: 2 monomer units

Level of theory: M06-2X(SMD=Water)/6-311+G(d,p)

Reactant

0 1

C	-0.002804	-0.001138	0.001710
C	0.000434	0.001762	1.515100
Cl	1.738992	0.006185	2.098163
C	-0.733765	1.198734	2.096993
C	-0.823506	1.149504	3.608668
Cl	-1.830563	2.522610	4.221731
H	0.446760	0.915732	-0.385432
H	-1.037036	-0.057337	-0.347099
H	0.542852	-0.859508	-0.390733
H	-0.407274	-0.927948	1.910872
H	-1.742984	1.182530	1.674590
H	-0.247854	2.122461	1.771205
H	-1.308959	0.238590	3.954026
H	0.146790	1.256350	4.086811

OH-

-1 1

O	0.000000	0.000000	-0.007018
H	0.000000	0.000000	0.954018

Transition State

-1 1

C	0.001994	0.000209	0.002035

C	0.000513	-0.001682	1.501221
C	1.326452	0.002003	2.080332
C	1.399902	-0.059508	3.584436
Cl	-1.628000	0.504315	-0.672343
Cl	2.418230	-1.633002	1.486235
O	-0.916336	2.340925	2.294581
H	1.991430	0.748534	1.649067
H	-0.638621	-0.786550	1.916213
H	0.830833	-0.909564	3.965627
H	2.428043	-0.128350	3.938022
H	0.957630	0.858628	3.984463
H	0.715410	0.718790	-0.401598
H	0.179662	-0.975671	-0.450553
H	-0.477383	1.219096	1.938899
H	-0.536622	2.477236	3.169192

Product

0 1

C	0.001183	0.000329	-0.004386
Cl	0.009516	0.011877	1.826394
C	1.389976	-0.000404	-0.532964
C	1.896028	1.020898	-1.222068
C	3.274507	1.057141	-1.799465
H	1.270397	1.896911	-1.387874
H	1.987150	-0.889793	-0.344348
H	3.820316	0.137369	-1.583415
H	3.234220	1.195131	-2.883525
H	3.836719	1.903073	-1.393892

H -0.553287 0.885722 -0.305431

H -0.549124 -0.899644 -0.269301

H2O

0 1

O 0.007886 0.000000 0.006105

H 0.010106 -0.000000 0.969057

H 0.940680 0.000000 -0.233012

Cl-

-1 1

Cl 0.000000 0.000000 0.000000

Model: 2 monomer units

Level of theory: M06-2X(SMD=Water)/6-31+G(d,p)

Reactant

0 1

C 0.000251 -0.004666 0.001561

C 0.001318 0.011257 1.516792

C 1.407871 0.011310 2.097540

C 1.416309 0.123331 3.610162

Cl 3.114078 0.262173 4.221967

Cl -0.914441 -1.457191 2.122366

H 0.541042 -0.877387 -0.375790

H 0.499785 0.899590 -0.360061

H	-1.018487	-0.018938	-0.391356
H	-0.571196	0.858773	1.899519
H	1.923905	0.877497	1.667657
H	1.940359	-0.890582	1.776456
H	0.893149	1.017792	3.950636
H	0.994122	-0.756578	4.093973

OH-

-1 1

O	0.000000	0.000000	-0.008722
H	0.000000	0.000000	0.955722

Transition State

-1 1

C	-0.008044	0.016105	0.016670
Cl	-0.009052	-0.200718	1.838214
C	1.383750	-0.010921	-0.543984
C	1.479501	0.538043	-1.881518
Cl	0.283333	-0.474257	-3.209955
C	2.841174	0.486303	-2.529310
O	2.833278	1.705869	0.837105
H	0.988852	1.506121	-1.993961
H	1.845262	-1.002127	-0.461882
H	3.239647	-0.531912	-2.515969
H	2.816053	0.848065	-3.558511
H	3.517246	1.128891	-1.953023
H	-0.497214	0.976403	-0.162211
H	-0.655691	-0.786787	-0.343835

H 2.163112 0.886298 0.166389

H 3.541780 1.991221 0.244688

Product

0 1

C -0.000000 -0.000000 0.000000

C 0.000000 0.000000 1.487786

C 1.125505 0.000000 2.207577

C 1.178818 -0.032167 3.702715

Cl -0.713397 1.555682 -0.650634

H 2.080827 0.020059 1.680891

H -0.971347 -0.015022 1.981405

H 0.175702 -0.051792 4.136640

H 1.728202 -0.913185 4.051283

H 1.709957 0.845231 4.087249

H 1.007541 -0.063230 -0.410171

H -0.626687 -0.786923 -0.419447

H2O

0 1

O 0.008781 0.000000 0.006798

H 0.006807 -0.000000 0.972395

H 0.943085 0.000000 -0.237042

Cl-

-1 1

Cl 0.000000 0.000000 0.000000

Model: 3 monomer units

Level of theory: ωB97X-D(SMD=Water)/6-31+G(d,p)

Reactant

0 1

C	1.447656	0.079972	-1.235176
C	0.391790	0.160843	-0.141234
C	-1.006370	-0.065611	-0.703767
C	-2.123759	-0.041843	0.335037
Cl	-3.706319	-0.300479	-0.557863
Cl	0.480700	1.795362	0.687529
C	2.887213	0.232226	-0.787473
H	1.260304	0.858699	-1.983998
H	1.320836	-0.886379	-1.735632
H	0.613749	-0.552904	0.653548
H	-0.991440	-1.052179	-1.182268
H	-1.205388	0.678787	-1.481215
C	-1.994564	-1.086010	1.426575
H	-2.229953	0.954208	0.766102
H	-1.118168	-0.862994	2.043737
H	-2.869489	-1.077452	2.080498
H	-1.874774	-2.087237	1.001569
Cl	3.393649	-1.081992	0.363207
H	3.561187	0.158779	-1.639700
H	3.064835	1.172056	-0.265234

Transition State

-1 1

C	-0.030768	-0.012045	0.029840
C	-0.009891	0.018922	1.543713
C	1.347650	0.012906	2.209825
C	1.344545	-0.032372	3.645789
C	2.689578	0.073250	4.327664
Cl	2.448292	-0.243669	6.138552
Cl	0.730625	-1.526728	-0.633619
C	3.757259	-0.873263	3.811923
Cl	2.256321	1.806884	1.492842
O	0.415582	-2.453610	4.111199
H	-0.573054	0.903364	1.861192
H	-0.552127	-0.854484	1.926009
H	2.069681	-0.639495	1.722705
H	0.849879	-1.299215	3.861923
H	0.615685	0.657558	4.085085
H	3.067718	1.099318	4.321445
H	4.022068	-0.594425	2.786836
H	4.665232	-0.808320	4.416399
H	3.401783	-1.908084	3.809891
H	-1.055203	-0.009944	-0.339938
H	0.522779	0.817017	-0.408139
H	-0.227554	-2.621009	3.412439

Product

0 1

C	0.006344	0.016802	0.019734
Cl	0.050256	0.018050	1.839545

C	1.398666	-0.012122	-0.592023
C	2.169417	-1.265379	-0.295487
C	2.541921	-2.141112	-1.231170
C	3.283016	-3.417309	-0.974705
C	3.588318	-3.753258	0.470180
Cl	4.872665	-3.342978	-1.922679
H	1.261454	0.095869	-1.674366
H	1.960041	0.863387	-0.244926
H	2.417246	-1.444640	0.749263
H	2.287882	-1.953453	-2.273789
H	2.757384	-4.245387	-1.453950
H	2.646473	-3.857910	1.017971
H	4.126954	-4.701011	0.534976
H	4.186740	-2.973776	0.949423
H	-0.526777	0.923831	-0.263290
H	-0.578433	-0.858544	-0.263890

Model: 3 monomer units

Level of theory: ωB97X-D(SMD=Water)/6-311+G(d,p)

Reactant

0 1

C	-0.001055	0.002229	0.003963
Cl	0.022362	0.059227	1.822080
C	1.392528	-0.003628	-0.584734
C	2.268316	-1.191799	-0.221487
Cl	1.480351	-2.743563	-0.804856

C	3.660811	-1.056340	-0.819266
C	4.615691	-2.192565	-0.475430
C	4.857890	-2.387712	1.005825
Cl	6.213881	-1.830292	-1.302255
H	1.283472	0.050368	-1.673184
H	1.925508	0.898812	-0.269589
H	2.316739	-1.313244	0.859671
H	4.073924	-0.119519	-0.429670
H	3.576759	-0.956223	-1.904702
H	4.293905	-3.122952	-0.940022
H	3.934372	-2.724790	1.485291
H	5.617668	-3.151133	1.180296
H	5.173266	-1.453955	1.478734
H	-0.546822	0.887725	-0.312344
H	-0.569705	-0.887737	-0.257337

Transition State

-1 1

C	-0.057668	0.121067	-0.036631
C	-0.042044	0.080297	1.474730
C	1.310380	0.025199	2.144178
C	1.300043	-0.062398	3.574149
C	2.637991	-0.025146	4.270082
Cl	2.371483	-0.472870	6.053287
Cl	0.691710	-1.368790	-0.767496
C	3.694296	-0.948781	3.700330
Cl	2.262138	1.821732	1.490025
O	0.332287	-2.479384	3.953043

H	-0.594325	0.954544	1.832891
H	-0.594578	-0.802729	1.814006
H	2.021495	-0.622600	1.639581
H	0.787645	-1.318296	3.745075
H	0.583913	0.623842	4.034896
H	3.029386	0.990644	4.348883
H	3.974002	-0.602949	2.701129
H	4.595101	-0.942458	4.316454
H	3.321301	-1.973343	3.621748
H	-1.078453	0.148451	-0.410394
H	0.506198	0.960967	-0.434219
H	0.785972	-2.753543	4.754795

Product

0 1

C	0.003816	0.001788	0.004748
C	0.001703	0.001365	1.523438
C	1.371120	0.002052	2.132980
C	1.851398	1.005062	2.862740
C	3.221285	1.057533	3.459547
Cl	3.022470	1.215258	5.294882
Cl	0.727667	-1.520458	-0.683184
C	4.142853	-0.104291	3.164961
H	-0.545229	0.898210	1.832525
H	-0.565128	-0.865369	1.879546
H	1.984069	-0.875919	1.944279
H	1.232200	1.880929	3.045729
H	3.698148	2.000454	3.192663

H	4.309747	-0.162003	2.085783
H	5.108304	0.043137	3.650915
H	3.718681	-1.052159	3.503133
H	-1.008617	0.048601	-0.390206
H	0.596680	0.820236	-0.399719

Model: 3 monomer units

Level of theory: ωB97X-D(SMD=Water)/def2-TZVPPD

Reactant

0 1

C	0.000000	0.000000	0.000000
Cl	0.000000	0.000000	1.807869
C	1.397731	0.000000	-0.572852
C	2.258174	-1.203353	-0.233460
Cl	1.469472	-2.724615	-0.858230
C	3.655137	-1.064280	-0.814995
C	4.606057	-2.199095	-0.466867
C	4.878662	-2.361410	1.010948
Cl	6.179657	-1.880098	-1.331121
H	1.302576	0.084938	-1.658249
H	1.932589	0.886976	-0.227085
H	2.296114	-1.347397	0.843220
H	4.065363	-0.129879	-0.423691
H	3.580593	-0.963646	-1.898458
H	4.259816	-3.134990	-0.896697
H	3.962303	-2.662418	1.521343

H	5.624342	-3.134992	1.186036
H	5.226595	-1.425295	1.449246
H	-0.534247	0.896672	-0.297667
H	-0.571071	-0.874206	-0.298305

Transition State

-1 1

C	0.004259	-0.000013	-0.002218
C	0.003095	-0.002341	1.507538
C	1.349141	-0.003179	2.189422
C	1.323394	-0.087256	3.620824
C	2.651522	0.007111	4.325466
Cl	2.387261	-0.352574	6.114591
Cl	0.783262	-1.484621	-0.684414
C	3.728724	-0.918902	3.805433
Cl	2.235852	1.779234	1.532252
O	0.403925	-2.527123	4.011567
H	-0.574167	0.863891	1.837486
H	-0.531678	-0.888135	1.859670
H	2.074875	-0.645090	1.702843
H	0.825715	-1.380343	3.801600
H	0.586918	0.585221	4.064629
H	3.027254	1.029828	4.352685
H	4.003741	-0.619911	2.792569
H	4.624981	-0.861898	4.421376
H	3.380635	-1.952023	3.777940
H	-1.010457	0.002708	-0.387625
H	0.555300	0.839866	-0.412386

H	-0.223282	-2.676179	3.301690

Product

0 1

C	0.005300	-0.000074	0.006630
C	0.006479	0.001948	1.523434
C	1.373976	0.005788	2.129961
C	1.852008	1.002950	2.862313
C	3.219659	1.056117	3.458847
Cl	3.023539	1.221545	5.281598
Cl	0.732629	-1.507457	-0.680071
C	4.137791	-0.105817	3.167384
H	-0.541487	0.894768	1.833640
H	-0.555616	-0.865039	1.879106
H	1.987844	-0.867180	1.935445
H	1.232112	1.874046	3.051225
H	3.697690	1.994090	3.184470
H	4.305013	-0.168297	2.090989
H	5.100655	0.040771	3.653178
H	3.712574	-1.049458	3.508080
H	-1.007111	0.042970	-0.383210
H	0.588112	0.822756	-0.398258

Model: 4 monomer units

Level of theory: ωB97X-D(SMD=Water)/6-31+G(d,p)

Reactant

0 1

C	4.014084	0.036647	-0.136099
Cl	3.804792	1.796091	-0.545438
C	2.849945	-0.806381	-0.615675
C	1.489185	-0.476662	-0.017170
Cl	1.539413	-0.695719	1.802977
C	0.399130	-1.354870	-0.621652
C	-1.011630	-1.093696	-0.099471
Cl	-2.115620	-2.337898	-0.868725
C	-1.519877	0.310398	-0.401767
C	-2.928877	0.599889	0.108117
C	-3.093843	0.463070	1.608950
Cl	-3.347277	2.316810	-0.387018
H	-1.467488	0.485379	-1.481081
H	-0.834455	1.015278	0.082696
H	-1.068328	-1.314554	0.966730
H	0.416681	-1.175759	-1.703048
H	0.656467	-2.405390	-0.454460
H	1.265870	0.582444	-0.151994
H	3.100766	-1.852047	-0.401363
H	2.755125	-0.713131	-1.703132
H	-3.665512	-0.007633	-0.418369
H	4.936199	-0.276175	-0.623755
H	4.143969	-0.005967	0.944919
H	-2.345158	1.057009	2.142202
H	-4.091237	0.778941	1.922866
H	-2.973840	-0.586597	1.895833

Transition State

-1 1

C	-0.049941	0.034980	-0.070018
Cl	-0.221285	0.197821	1.734929
C	1.400364	-0.011852	-0.503793
C	2.248353	1.201499	-0.192187
C	3.633693	1.105832	-0.566091
C	4.483475	2.343914	-0.380231
Cl	6.240936	1.888389	-0.747343
C	4.398434	2.955819	1.013650
C	5.277435	4.183351	1.232056
C	4.982959	5.343661	0.301889
Cl	5.031286	4.733481	2.968171
Cl	1.278295	2.777723	-1.231570
O	4.547154	-0.711147	1.099629
H	4.634699	2.188837	1.758158
H	3.356153	3.259014	1.165538
H	4.268274	3.095794	-1.143732
H	4.092280	0.147029	0.314438
H	3.765863	0.690606	-1.570988
H	2.054073	1.619562	0.793287
H	1.412380	-0.203700	-1.582422
H	1.889922	-0.867947	-0.024414
H	6.334163	3.917773	1.194635
H	-0.558305	-0.891673	-0.333243
H	-0.581935	0.883390	-0.497408
H	3.920633	5.605879	0.324609
H	5.573935	6.221990	0.571398

H	5.249800	5.065739	-0.722785
H	5.379585	-0.328000	1.400205

Product

0	1		
C	0.108295	-0.137268	-0.043264
C	0.027484	0.182749	1.441568
C	1.303260	-0.073119	2.189557
C	1.426241	-1.008451	3.133296
C	2.679061	-1.331916	3.889403
C	3.920569	-0.558250	3.469677
C	5.188589	-0.940570	4.228703
Cl	6.541601	0.125841	3.595297
Cl	1.284927	0.939262	-0.920803
Cl	2.334305	-1.047774	5.684312
C	5.599640	-2.393328	4.091718
H	3.739350	0.514773	3.580241
H	4.074147	-0.765483	2.404103
H	2.853538	-2.408196	3.840736
H	0.565929	-1.622882	3.395448
H	2.154100	0.548508	1.917386
H	-0.776433	-0.442700	1.847069
H	-0.276381	1.228526	1.567075
H	5.109308	-0.660577	5.279658
H	-0.853716	0.018580	-0.530063
H	0.449286	-1.157857	-0.218590
H	5.667582	-2.686082	3.039508
H	6.562005	-2.573696	4.575879

H 4.857999 -3.031167 4.583304

Model: 4 monomer units

Level of theory: ωB97X-D(SMD=Water)/6-311+G(d,p)

Reactant

0 1

C -0.001410 -0.017048 0.005024

Cl 0.028849 -0.087077 1.822378

C 1.390398 0.001969 -0.587586

C 2.261093 1.190842 -0.214171

Cl 1.467977 2.745035 -0.780969

C 3.651859 1.063349 -0.819365

C 4.608118 2.204116 -0.491649

Cl 6.164338 1.889110 -1.406968

C 4.899286 2.342360 0.995023

C 5.851025 3.477256 1.352429

C 5.374237 4.851380 0.933478

Cl 6.072797 3.448892 3.174177

H 5.287488 1.392562 1.372711

H 3.944706 2.532945 1.496407

H 4.243708 3.138808 -0.913596

H 4.073269 0.126310 -0.440314

H 3.558911 0.970164 -1.904505

H 2.307229 1.299618 0.868131

H 1.278996 -0.041289 -1.676263

H 1.928707 -0.900716 -0.282558

H	6.851534	3.281115	0.971319
H	-0.541761	-0.904080	-0.316379
H	-0.577244	0.870564	-0.247909
H	4.363359	5.044893	1.302106
H	6.045133	5.627748	1.304428
H	5.364085	4.917585	-0.158198

Transition State

-1 1

C	-0.052914	0.034453	-0.080677
Cl	-0.236944	0.201470	1.723264
C	1.399212	-0.007278	-0.500475
C	2.235002	1.211325	-0.185769
C	3.623411	1.122224	-0.538838
C	4.461604	2.363674	-0.348300
Cl	6.232719	1.907448	-0.651021
C	4.332183	2.999059	1.029033
C	5.199335	4.231178	1.251872
C	4.938685	5.367978	0.287225
Cl	4.885797	4.818855	2.965023
Cl	1.273021	2.773028	-1.244153
O	4.522778	-0.664375	1.166846
H	4.546176	2.246453	1.792705
H	3.286063	3.301487	1.142619
H	4.274009	3.099641	-1.131532
H	4.070903	0.178002	0.360620
H	3.774785	0.696794	-1.534961
H	2.024354	1.634649	0.792020

H	1.424554	-0.203447	-1.576812
H	1.888126	-0.857416	-0.012736
H	6.255377	3.968484	1.264490
H	-0.556174	-0.893501	-0.341891
H	-0.585090	0.879017	-0.510767
H	3.876988	5.628139	0.265279
H	5.518067	6.252353	0.557250
H	5.242101	5.067280	-0.719576
H	5.347623	-0.268680	1.461779

Product

0 1

C	0.006428	0.002949	-0.000905
Cl	0.012078	0.002006	1.819571
C	1.410208	0.003381	-0.580452
C	2.194414	1.242128	-0.268397
C	2.582771	2.115713	-1.193003
C	3.336528	3.382326	-0.937230
Cl	4.935242	3.269842	-1.860682
C	3.602885	3.708363	0.522784
C	4.339564	5.023170	0.750381
C	3.631935	6.250173	0.216898
Cl	4.571140	5.206512	2.562089
H	4.162813	2.891808	0.984493
H	2.626060	3.764913	1.014832
H	2.826469	4.205457	-1.436743
H	2.337276	1.936629	-2.237663
H	2.433288	1.409322	0.778717

H	1.296967	-0.104145	-1.664206
H	1.947513	-0.879431	-0.218627
H	5.357220	4.967643	0.367924
H	-0.539157	-0.891790	-0.291944
H	-0.553187	0.889195	-0.294880
H	2.605302	6.304616	0.588495
H	4.162965	7.160520	0.499182
H	3.604092	6.209907	-0.875760

Model: 4 monomer units

Level of theory: ωB97X-D(SMD=Water)/def2-TZVPPD

Reactant

0 1

C	3.997119	0.053248	-0.158470
Cl	3.770618	1.811490	-0.513097
C	2.837873	-0.783520	-0.646172
C	1.486561	-0.477317	-0.026860
Cl	1.556638	-0.732831	1.776926
C	0.396680	-1.344774	-0.635299
C	-1.005965	-1.089041	-0.103601
Cl	-2.107950	-2.333683	-0.847547
C	-1.521493	0.307301	-0.407282
C	-2.915042	0.599715	0.127707
C	-3.044436	0.495912	1.629992
Cl	-3.355882	2.291119	-0.392885
H	-1.494575	0.469050	-1.485583

H	-0.828670	1.017513	0.049723
H	-1.049719	-1.302218	0.960486
H	0.407590	-1.156376	-1.711460
H	0.653596	-2.393388	-0.481694
H	1.256587	0.579026	-0.135661
H	3.093854	-1.829898	-0.462180
H	2.731888	-0.663745	-1.726334
H	-3.655762	-0.023712	-0.365135
H	4.914099	-0.236330	-0.661637
H	4.138546	-0.018461	0.915749
H	-2.296466	1.112603	2.129865
H	-4.035952	0.803930	1.957064
H	-2.901007	-0.540741	1.938962

Transition State

-1 1

C	-0.016653	-0.090025	-0.026688
C	0.017125	0.055295	1.475814
C	1.375614	0.042580	2.133129
C	1.374401	0.235232	3.555017
C	2.698801	0.125090	4.266933
C	3.804968	0.973789	3.660884
C	5.142742	0.892931	4.379048
Cl	6.296821	2.017290	3.519596
Cl	0.847732	1.262039	-0.863522
Cl	2.442138	0.619877	6.023662
C	5.749208	-0.490618	4.425519
Cl	2.175183	-1.815096	1.610598

O	0.587445	2.730205	3.825354
H	3.472066	2.011196	3.609929
H	3.953840	0.623055	2.637141
H	3.021996	-0.910663	4.361278
H	0.948674	1.560419	3.671599
H	0.615721	-0.370482	4.053689
H	2.114695	0.616113	1.585751
H	-0.601050	-0.740939	1.895973
H	-0.456959	1.000287	1.752107
H	5.071352	1.313614	5.377887
H	-1.038347	-0.057028	-0.392010
H	0.464181	-1.002431	-0.363408
H	5.820222	-0.919943	3.425280
H	6.741118	-0.467264	4.873669
H	5.123048	-1.142366	5.036823
H	1.055241	3.000559	4.617828

Product

0	1		
C	0.005239	0.014343	-0.002478
Cl	-0.000294	0.029200	1.806436
C	1.409445	0.011036	-0.575972
C	2.192598	1.247885	-0.268172
C	2.595814	2.109284	-1.192354
C	3.350853	3.373309	-0.939653
Cl	4.941455	3.255365	-1.852716
C	3.611193	3.704614	0.517762
C	4.338582	5.021923	0.742923

C	3.611781	6.244165	0.230815
Cl	4.601672	5.196562	2.539214
H	4.174791	2.894773	0.980891
H	2.636964	3.755587	1.009925
H	2.842123	4.194009	-1.440200
H	2.364415	1.921855	-2.236292
H	2.417507	1.423848	0.778043
H	1.302803	-0.103534	-1.657205
H	1.942179	-0.868100	-0.205694
H	5.345636	4.977993	0.337572
H	-0.536748	-0.880762	-0.291616
H	-0.553004	0.894604	-0.309346
H	2.597782	6.292524	0.629458
H	4.144124	7.154192	0.501791
H	3.553903	6.206532	-0.858258

Model: 5 monomer units

Level of theory: ωB97X-D(SMD=Water)/6-31+G(d,p)

Reactant

0 1

C	-0.000000	-0.000000	0.000000
C	0.000000	-0.000000	1.515867
C	1.408059	-0.000000	2.091805
C	1.528183	0.047159	3.607332
C	2.972605	0.036178	4.102449
C	3.747699	-1.238274	3.786917

C	5.189193	-1.212068	4.289907
C	6.078601	-0.144051	3.662663
Cl	6.134533	-0.358142	1.842243
Cl	-0.918664	-1.473807	2.117187
Cl	0.739555	1.572799	4.245606
Cl	2.923496	-2.676756	4.567369
C	7.488099	-0.204480	4.235294
C	8.458851	0.845801	3.734956
Cl	7.923950	2.532941	4.151376
H	5.644339	-2.193435	4.124306
H	5.187162	-1.023490	5.369863
H	3.725081	-1.468307	2.721606
H	3.501122	0.872108	3.630611
H	2.992216	0.201537	5.183971
H	0.956163	-0.757682	4.070330
H	1.934114	0.861594	1.663052
H	1.925031	-0.899200	1.737759
H	5.660399	0.853816	3.801233
H	-0.578083	0.842271	1.897598
H	7.396622	-0.128755	5.324421
H	7.931890	-1.182672	4.015153
H	9.433372	0.717255	4.203693
H	8.573326	0.826797	2.651448
H	-1.018301	-0.008719	-0.395172
H	0.496346	0.911294	-0.349305
H	0.543629	-0.863717	-0.394333

Transition State

-1 1

C	0.035706	0.063773	-0.021040
C	0.025722	-0.053865	1.490535
C	1.417114	0.081898	2.089692
C	1.532456	0.021879	3.606388
C	2.957102	0.135086	4.122247
C	3.840426	-0.941437	3.743223
C	5.225144	-0.958016	4.364353
C	6.173738	0.089298	3.790100
Cl	6.482040	-0.262832	2.014111
Cl	-0.709396	-1.674527	1.956347
Cl	0.523954	1.375134	4.352148
Cl	3.080686	-2.803911	4.373725
C	7.492778	0.125590	4.547122
C	8.490605	1.171422	4.092420
Cl	7.841843	2.861321	4.271615
H	5.681389	-1.944423	4.250674
H	5.135849	-0.752584	5.437148
H	3.846559	-1.202860	2.687242
H	3.478492	1.306770	3.584289
H	2.965002	0.292259	5.206618
H	1.042723	-0.878660	3.987410
H	1.825087	1.035797	1.735760
H	2.051299	-0.710171	1.674602
H	5.705879	1.072749	3.779062
H	-0.658412	0.675304	1.926120
H	7.252802	0.287205	5.603832
H	7.990665	-0.848845	4.474085

H	9.392060	1.131263	4.702345
H	8.758379	1.064138	3.041650
H	-0.970186	-0.041916	-0.433911
H	0.416189	1.054150	-0.291774
H	0.687136	-0.691645	-0.470793
O	3.832695	2.404407	3.109066
H	4.382892	2.809335	3.789980

Product

0 1

C	-0.107345	-0.166933	0.032481
C	-0.030162	0.012523	1.535999
C	1.401459	-0.045046	2.047782
C	1.594560	0.148507	3.542244
C	3.005632	0.055340	4.037808
C	4.090421	-0.091684	3.274739
C	5.480165	-0.195666	3.831067
C	6.377019	0.991314	3.484585
Cl	6.585506	1.109226	1.664935
Cl	-1.041813	-1.290510	2.346427
Cl	0.938402	1.799699	4.054319
C	7.739613	0.885392	4.153691
C	8.699323	2.033078	3.914089
Cl	8.058132	3.612938	4.547416
H	5.961135	-1.116607	3.479541
H	5.437392	-0.243278	4.925107
H	3.997589	-0.147387	2.192286
H	3.112671	0.104350	5.120544

H	0.967370	-0.547117	4.103108
H	1.963769	0.719273	1.499281
H	1.832978	-1.018019	1.784912
H	5.881358	1.925739	3.755054
H	-0.514616	0.942741	1.835210
H	7.562736	0.775589	5.229454
H	8.242797	-0.028166	3.814517
H	9.638085	1.860267	4.438332
H	8.900294	2.194748	2.855426
H	-1.141476	-0.128809	-0.317084
H	0.447450	0.646819	-0.445791
H	0.338551	-1.117742	-0.274290

Model: 5 monomer units

Level of theory: ωB97X-D(SMD=Water)/6-311+G(d,p)

Reactant

0 1

C	-0.000107	-0.000030	0.000118
C	-0.000066	0.000202	1.513397
C	1.404879	-0.000080	2.090415
C	1.520699	0.055645	3.603666
C	2.960481	0.029201	4.103239
C	3.717077	-1.255707	3.797181
C	5.160634	-1.238997	4.285967
C	6.050083	-0.188985	3.635037
Cl	6.087072	-0.435328	1.817350

Cl	-0.915333	-1.476869	2.114384
Cl	0.750076	1.596569	4.227387
Cl	2.881372	-2.673835	4.601941
C	7.462690	-0.247462	4.193170
C	8.431801	0.786764	3.664267
Cl	7.907178	2.483236	4.057398
H	5.605494	-2.225043	4.129515
H	5.171347	-1.036155	5.362113
H	3.681474	-1.501199	2.737813
H	3.501364	0.854817	3.629973
H	2.979853	0.199354	5.182654
H	0.935240	-0.733759	4.071673
H	1.935336	0.855915	1.659076
H	1.917722	-0.902117	1.741546
H	5.638427	0.811796	3.755309
H	-0.581154	0.837072	1.897023
H	7.383515	-0.151467	5.280486
H	7.896552	-1.231778	3.987077
H	9.409454	0.665555	4.124200
H	8.533075	0.751143	2.581679
H	-1.016977	-0.012191	-0.395287
H	0.493196	0.911779	-0.348982
H	0.546657	-0.860809	-0.393100

Transition State

-1 1

C	0.033028	0.102952	-0.022651
C	0.030094	-0.059084	1.482246

C	1.415754	0.095822	2.083679
C	1.530651	0.004473	3.596571
C	2.949136	0.132987	4.116913
C	3.855511	-0.909019	3.706836
C	5.235699	-0.914536	4.333327
C	6.158293	0.173388	3.801248
Cl	6.492081	-0.118517	2.018253
Cl	-0.656997	-1.714229	1.900528
Cl	0.496906	1.323803	4.369734
C	7.467839	0.225768	4.568775
C	8.429923	1.319186	4.159018
Cl	7.720117	2.977213	4.400108
Cl	3.136886	-2.804129	4.268875
O	3.771752	2.442289	3.150531
H	5.716411	-1.883495	4.188502
H	5.136633	-0.749258	5.410955
H	3.871495	-1.135774	2.644741
H	3.443425	1.328845	3.605480
H	2.954536	0.260090	5.203607
H	1.054852	-0.908672	3.958991
H	1.802216	1.065393	1.753143
H	2.067181	-0.670428	1.650625
H	5.664194	1.141510	3.810056
H	-0.673937	0.632578	1.941893
H	7.216242	0.342197	5.627496
H	7.996601	-0.728071	4.466210
H	9.328657	1.290709	4.770421
H	8.702881	1.264631	3.107359

H	-0.968946	-0.019608	-0.437194
H	0.383977	1.110454	-0.264447
H	0.705102	-0.618573	-0.494338
H	4.297983	2.848293	3.845030

Product

0	1		
C	-0.008689	-0.011338	-0.003784
C	-0.006516	0.006283	1.509626
C	1.400254	-0.005244	2.082634
C	1.514515	0.040298	3.594425
C	2.903304	-0.004782	4.148043
C	4.023740	0.006542	3.431593
C	5.390777	-0.050572	4.042883
C	6.194642	1.234321	3.874954
Cl	6.469318	1.570711	2.091009
Cl	-0.946573	-1.449304	2.124803
Cl	0.717671	1.579177	4.239977
C	7.530038	1.166123	4.596193
C	8.392182	2.407574	4.533422
Cl	7.585976	3.844315	5.305353
H	5.962055	-0.882881	3.617418
H	5.306419	-0.226024	5.119948
H	3.981024	0.057837	2.347196
H	2.959739	-0.062103	5.232907
H	0.916263	-0.748305	4.050338
H	1.926946	0.849510	1.646235
H	1.913277	-0.910488	1.741189

H	5.609335	2.088929	4.213850
H	-0.574728	0.855861	1.884666
H	7.319479	0.920964	5.641913
H	8.123072	0.341550	4.185708
H	9.318647	2.258334	5.082467
H	8.619032	2.708302	3.512902
H	-1.026324	-0.009915	-0.397258
H	0.500359	0.887116	-0.364541
H	0.521519	-0.886573	-0.387528

Model: 5 monomer units

Level of theory: ωB97X-D(SMD=Water)/def2-TZVPPD

Reactant

0 1

C	-0.001302	-0.000562	0.000006
C	-0.000097	0.000190	1.511103
Cl	1.726368	0.001386	2.107904
C	-0.744085	1.190120	2.085668
C	-0.849717	1.259690	3.596518
Cl	-1.734530	-0.204128	4.221787
C	-1.589678	2.491583	4.097274
C	-0.904209	3.814375	3.796152
Cl	0.731364	3.858725	4.595259
C	-1.686872	5.024031	4.285671
C	-3.034054	5.236919	3.614371
C	-3.745145	6.447167	4.191422

C	-5.126325	6.726961	3.647641
Cl	-6.283138	5.380505	3.989482
Cl	-2.812544	5.444833	1.816879
H	-1.081352	5.920884	4.151233
H	-1.880779	4.913403	5.355234
H	-0.682283	3.916198	2.738037
H	-2.575139	2.513382	3.627085
H	-1.742754	2.413749	5.173996
H	0.131614	1.189543	4.057362
H	-1.749606	1.184370	1.657094
H	-0.254353	2.101775	1.736228
H	-3.663970	4.355882	3.703003
H	-0.406821	-0.932258	1.892808
H	-3.801644	6.303208	5.272331
H	-3.141172	7.341116	4.017290
H	-5.549566	7.609097	4.117277
H	-5.130228	6.857143	2.569501
H	0.545164	-0.855644	-0.394138
H	-1.033420	-0.061919	-0.349565
H	0.441303	0.915571	-0.392302

Transition State

-1 1

C	-0.088450	-0.006620	-0.009685
C	0.023595	0.059427	1.496132
Cl	1.779313	0.293781	1.948995
C	-0.823405	1.168471	2.089008
C	-0.833504	1.298802	3.600974

Cl	-1.456264	-0.259413	4.342992
C	-1.670085	2.451045	4.115988
C	-1.215482	3.764208	3.737603
C	-1.927970	4.947005	4.358024
C	-3.312295	5.208653	3.786767
C	-4.031685	6.307966	4.544327
C	-5.444311	6.600915	4.096196
Cl	-6.532021	5.169077	4.289513
Cl	-3.176127	5.656586	2.022278
Cl	0.743229	4.093502	4.339839
O	-4.064780	2.004783	3.103786
H	-1.329484	5.849814	4.247099
H	-2.054779	4.762895	5.427258
H	-1.013721	3.905405	2.682097
H	-2.958330	2.276062	3.574863
H	-1.804038	2.375170	5.196802
H	0.187726	1.348390	3.978000
H	-1.845592	1.013295	1.736251
H	-0.485524	2.120530	1.672839
H	-3.904057	4.299343	3.775030
H	-0.230899	-0.899304	1.939702
H	-4.038281	6.021868	5.598124
H	-3.466200	7.240206	4.468169
H	-5.882177	7.390419	4.698745
H	-5.498615	6.876069	3.047143
H	0.529998	-0.804274	-0.417995
H	-1.127832	-0.207711	-0.275250
H	0.205898	0.939216	-0.465879

H	-4.690261	2.267274	3.781830

Product

0 1

C	-4.450972	-1.676105	-1.406928
C	-4.042270	-0.407522	-0.694486
C	-2.618431	-0.474958	-0.176465
C	-2.100555	0.762757	0.525135
C	-0.711274	0.675199	1.066769
C	0.114517	-0.351740	0.917290
C	1.494853	-0.389255	1.491679
C	2.601241	-0.377334	0.445253
Cl	2.473292	-1.856533	-0.614507
Cl	-5.198595	-0.101591	0.686286
Cl	-2.148709	2.200544	-0.618044
C	3.977486	-0.315647	1.080071
C	5.149347	-0.246708	0.129576
Cl	5.115512	1.242155	-0.895780
H	1.617750	-1.274859	2.120675
H	1.654889	0.486544	2.124193
H	-0.196002	-1.225374	0.355590
H	-0.390049	1.542881	1.634418
H	-2.780011	1.062030	1.320325
H	-1.979896	-0.709085	-1.031228
H	-2.537051	-1.309411	0.524229
H	2.454573	0.452765	-0.242207
H	-4.177998	0.454050	-1.342567
H	3.990730	0.555959	1.737896

H	4.125289	-1.195775	1.711204
H	6.084519	-0.208293	0.678997
H	5.172670	-1.083972	-0.561498
H	-5.476301	-1.612487	-1.767123
H	-3.793774	-1.823487	-2.265719
H	-4.358475	-2.541392	-0.749787

We present the cartesian coordinates of optimized stationary points of the reaction with the inclusion of an explicit water molecule. The Reactant is a PVC model, which reacts with a hydroxide ion and a water molecule, forming the studied E2 Transition State. From the Transition State, a H_2O dimer, Cl^-, and the Product are formed.

Model: 2 monomer units including an explicit water molecule

Level of theory: ωB97X-D(SMD=Water)/6-31+G(d,p)

Reactant

0 1

C	-0.013515	-0.007895	-0.008429
C	-0.019678	0.012715	1.507536
Cl	1.717084	-0.027622	2.112003
C	-0.739534	1.230866	2.072149
C	-0.864225	1.196866	3.584202
Cl	-1.856680	2.595380	4.177436
H	0.452733	0.896026	-0.411624
H	-1.048663	-0.052186	-0.362117
H	0.517317	-0.883200	-0.389687
H	-0.455960	-0.906255	1.903967
H	-1.740952	1.229491	1.627318
H	-0.232387	2.145582	1.747600

H	-1.373955	0.295457	3.926415
H	0.100195	1.283969	4.083354

H2O

0 1

O	1.02113500	3.58631200	-0.14058100
H	1.63340900	2.92497800	0.19279200
H	0.35013500	3.07936700	-0.60550100

OH

-1 1

O	2.71965200	1.88944700	0.72517300
H	2.52456500	1.67997200	1.64094700

Transition State

-1 1

C	-0.088450	-0.006620	-0.009685
C	0.023595	0.059427	1.496132
Cl	1.779313	0.293781	1.948995
C	-0.823405	1.168471	2.089008
C	-0.833504	1.298802	3.600974
Cl	-1.456264	-0.259413	4.342992
C	-1.670085	2.451045	4.115988
C	-1.215482	3.764208	3.737603
C	-1.927970	4.947005	4.358024
C	-3.312295	5.208653	3.786767
C	-4.031685	6.307966	4.544327

C	-5.444311	6.600915	4.096196
Cl	-6.532021	5.169077	4.289513
Cl	-3.176127	5.656586	2.022278
Cl	0.743229	4.093502	4.339839
O	-4.064780	2.004783	3.103786
H	-1.329484	5.849814	4.247099
H	-2.054779	4.762895	5.427258
H	-1.013721	3.905405	2.682097
H	-2.958330	2.276062	3.574863
H	-1.804038	2.375170	5.196802
H	0.187726	1.348390	3.978000
H	-1.845592	1.013295	1.736251
H	-0.485524	2.120530	1.672839
H	-3.904057	4.299343	3.775030
H	-0.230899	-0.899304	1.939702
H	-4.038281	6.021868	5.598124
H	-3.466200	7.240206	4.468169
H	-5.882177	7.390419	4.698745
H	-5.498615	6.876069	3.047143
H	0.529998	-0.804274	-0.417995
H	-1.127832	-0.207711	-0.275250
H	0.205898	0.939216	-0.465879
H	-4.690261	2.267274	3.781830

Product

0	1		
C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.490952

C	1.087903	0.000000	2.251380
C	1.035954	0.033177	3.732546
Cl	1.695180	-1.517859	4.445647
H	-0.526768	0.875546	-0.385350
H	1.012594	-0.001290	-0.402408
H	-0.528018	-0.876343	-0.382286
H	-0.972706	0.004381	1.975432
H	2.073923	-0.008500	1.797946
H	1.661616	0.813965	4.154811
H	0.021976	0.124237	4.108997

H2O dimer

0 1

O	-0.936386	2.770470	2.424857
O	1.183984	3.472395	0.727426
H	-0.876695	1.858370	2.723668
H	-1.779627	2.822527	1.965495
H	0.447097	3.195215	1.301102
H	1.419704	2.683429	0.233328

Cl-

-1 1

Cl	0.000000	0.000000	0.000000

References

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