

The Mechanism of Monochloramine Disproportionation under acidic conditions

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Number of pages: 13

Number of figures: 3

Number of tables: 0

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List of contents

- Page S2: Details of the free energy methods used in the MD approach
- Page S3: Figure S1. The conversion of DCA into TCA under acidic condition
- Page S4: Derivation of the $[H^+]$ dependence of the observed rate constant
- Page S5: Estimation of the uncertainty in the MD-calculated free energies
- Page S8: Detailed analysis of the static DFT energy profile
- Page S9-S13: Cartesian coordinates of the static DFT structures

Details of the free energy methods used in the molecular dynamics approach

Along the reaction coordinate, first a steered dynamics run was performed to explore the reaction. Then thermodynamic integration (TI) simulations initiated at selected configurations of this trajectory have been conducted.¹ Typical production runs were 10 ps long, from which the first 2 ps were discarded to account for equilibration. Three different reactions have been studied with TI. In all cases the reaction coordinate (collective variable, CV) was a suitable atomic distance which allows to avoid technical difficulties associated with the blue-moon type samplings.² The transition states obtained from the simulations have been verified by committor analysis. In committor analysis, a large number of independent simulations are performed starting from randomly selected configurations taken from the TS ensemble with initial velocities taken from the Boltzmann distribution at 300 K. The committor is the probability of reaching first the product state (or the reactant state). Ideally the committor is 0.5 (i.e. from the TS the system goes to the reactant and products states with equal probabilities). In practice, for the dimer formation, 80 initial configurations from the TS have been selected. The trajectories were allowed to evolve for 2.5 ps, then we searched for the first occurrence of $d(\text{N Cl})$ outside the 2.40 to 3.80 Å interval where the former value represent the product (dimer) and the latter, the reactant states. This way we obtained a ratio of 54:46 which is very close to the ideal equal probabilities. In case of the other TS-s, the procedure was the same, but the number of initial states and the product ratios differ slightly.

References:

- (1) A. Pohorille and C. Chipot, *Free energy calculations: theory and applications in chemistry and biology*. Springer: Berlin, **2007**.
- (2) G. Ciccotti, R. Kapral and E. Vanden-Eijnden, *ChemPhysChem* **2005**, *6*, 1809–1814.

The conversion of DCA into TCA under acidic condition

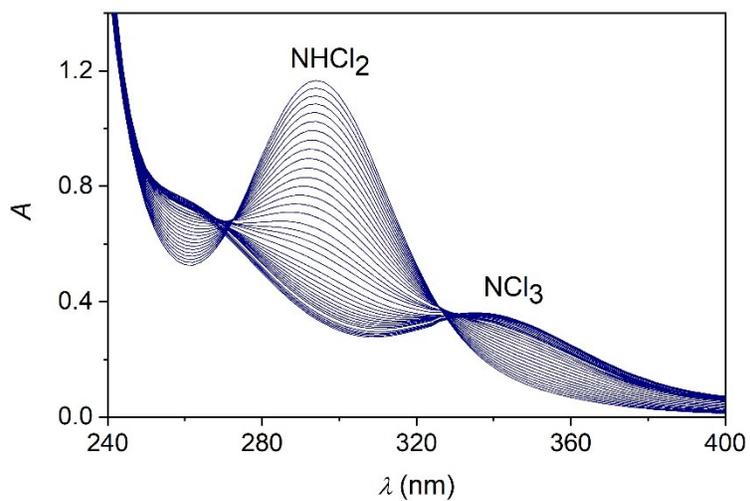


Figure S1. The conversion of DCA into TCA under acidic condition. $c_{\text{DCA}}^0 = 3.821 \times 10^{-3}$ M, pH = 1.97, reaction time 2.5 h, $I = 1.0$ M (NaClO₄), $T = 25.0$ °C

Derivation of the $[H^+]$ dependence of the observed rate constant for the MCA + PMCA reaction.

Step 1. We express the concentration of the MCA in terms of the pH and constants (total chloramine concentration, c_0 , and protonation constant, K_a).

$$\begin{aligned}
 NH_3Cl^+ &\rightleftharpoons NH_2Cl + H^+ \\
 K_a &= \frac{[H^+][NH_2Cl]}{[NH_3Cl^+]} = \frac{[H^+](c_0 - x)}{x} \\
 c_0[H^+]/K_a - x[H^+]/K_a &= x \\
 c_0[H^+]/K_a &= x([H^+]/K_a + 1) \\
 [NH_3Cl^+] &= x = \frac{c_0[H^+]/K_a}{1 + [H^+]/K_a} \\
 [NH_2Cl] &= c_0 - x = \frac{c_0}{1 + [H^+]/K_a}
 \end{aligned}$$

Step 2. Assuming a pre-equilibrium process, the observed rate constant can also be rewritten using the pH and other constants.

$$\begin{aligned}
 NH_2Cl + NH_3Cl^+ &\xrightleftharpoons{k} I \rightarrow P \\
 K &= \frac{[I]}{[NH_3Cl^+][NH_2Cl]} \\
 r &= \frac{d[P]}{dt} = k[I] = kK[NH_3Cl^+][NH_2Cl] \\
 r &= kKK_a^{-1}[NH_2Cl]^2[H^+] = kKK_a^{-1} \frac{c_0^2}{(1 + [H^+]/K_a)^2} [H^+] \\
 k_{app} &= kKK_a^{-1} \frac{[H^+]}{(1 + [H^+]/K_a)^2}
 \end{aligned}$$

Expression of the time-dependent absorbance in stopped-flow measurements.

Step 1. We first write down the rate equation for the disproportion process.

$$2A = B + D$$

$$\frac{dc_A}{dt} = -kc_A^2$$

$$\frac{1}{c_A} = \frac{1}{c_A^0} + kt$$

Step 2. We express the concentrations of A (monochloramine) and B (dichloramine).

$$c_A = \frac{c_A^0}{1 + ktc_A^0}$$

$$\Delta c_A = c_A^0 - \frac{c_A^0}{1 + ktc_A^0}$$

$$c_B = \frac{1}{2}\Delta c_A$$

Step 3. We use these expressions in the Beer-Lambert law to obtain the time dependence of the absorbance. It is important to note that this way the two absorbing species (mono- and dichloramine) are measured simultaneously using any wavelength. The selected 250 and 300 nm values were simply chosen so that the largest changes (see Fig. 3) can be observed.

$$Abs = c_A \varepsilon_A + c_B \varepsilon_B + const$$

$$Abs = \frac{c_A^0}{1 + ktc_A^0} \varepsilon_A + \frac{1}{2} c_A^0 \varepsilon_B - \frac{c_A^0}{1 + ktc_A^0} \varepsilon_B + const$$

$$Abs = \frac{1}{2} c_A^0 \varepsilon_B + \frac{c_A^0 \left(\varepsilon_A - \frac{1}{2} \varepsilon_B \right)}{1 + ktc_A^0} + const$$

$$Abs = \alpha + \frac{\beta}{1 + \gamma t}$$

Estimation of the uncertainty in the free energies calculated by MD

After performing constrained MD simulations, at each λ_i value of the collective variable (CV, an N–Cl or N–H bond length in our case) we obtained a set of Lagrangian multipliers ($dU/d\lambda$). Therefore, at each λ_i , we can calculate the averages of the corresponding forces which are then integrated over λ to yield the free energy profile.¹

$$x_i = \left\langle \frac{dU}{d\lambda_i} \right\rangle \quad (1)$$

$$\sigma_i = st.dev\left(\frac{dU}{d\lambda_i}\right) \quad (2)$$

From the sample average and standard deviation, the standard error of the mean (SE) can be derived using the block-averaging technique which accounts for the correlation of the Lagrangian multipliers in successive time frames during a single simulation. Among the many ways to visualize and analyze these results,² we chose a very simple approach, which is to plot the SE vs the block lengths, using the block variances.

$$SE = \frac{\sqrt{\sigma_b^2}}{\sqrt{N_b}} = \frac{\sqrt{\sigma_b^2}}{\sqrt{\tau_{sim}/\tau}} \quad (3)$$

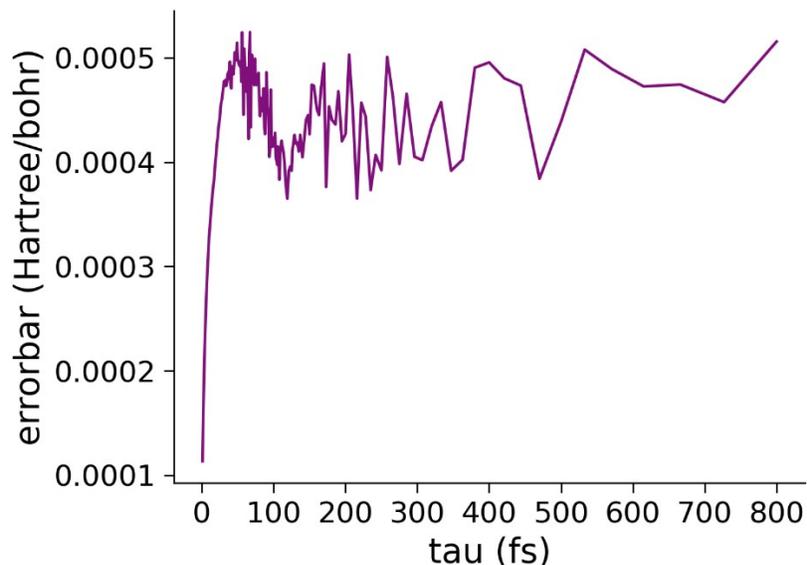


Figure S2. A typical standard error vs τ curve.

The SE usually converges to a value SE_{conv} after a block length of 200 fs (Fig. 1). The estimation of SE_{conv} was done with the naked eye and thus may contain error. Using $1.96 \cdot SE_{\text{conv},i}$, we defined a 95% confidence interval for x_i . This was then used to obtain the shaded areas (error band on Figs. 8 and 10) on the free energy figures with the following approach:

1. At each λ_i , a random number was drawn from the interval $x_i \pm 1.96 \cdot SE_{\text{conv},i}$. Note that drawing from the $N(x_i, SE_i^2)$ distribution instead of the uniform sampling of $x_i \pm 1.96 \cdot SE_{\text{conv},i}$ yields the same result.
2. The obtained x_i' values were integrated (trapezoid method) over λ in the same way as the average x_i values, providing a new free energy profile.
3. The previous two tasks were repeated 10000 times and their SE_i' was calculated at each λ_i .
4. Task 3 was repeated 25 times and the obtained 25 SE_i' values were averaged.
5. The upper and lower error curves were plotted using $\Delta A_i \pm 1.96 \cdot \langle SE_i' \rangle$ and the area between them was shaded.

(1) Pohorille, A. and Chipot, C. *Free energy calculations: theory and applications in chemistry and biology*. Springer: Berlin, **2007**.

(2) (a) <https://plumed.github.io/doc-v2.4/user-doc/html/trieste-2.html> (b) Yang, W.; Bitetti-Putzer, R.; Karplus, M. Free Energy Simulations: Use of Reverse Cumulative Averaging to Determine the

Equilibrated Region and the Time Required for Convergence. *J. Chem. Phys.* **2004**, *120*, 2618–2628. (c) Straatsma, T. P.; Berendsen, H. J. C.; Stam, A. J. Estimation of Statistical Errors in Molecular Simulation Calculations. *Mol. Phys.* **1986**, *57*, 89–95. (d) Guardia, E.; Rey, R.; Padro, J. A. Statistical Errors in Constrained Molecular Dynamics Calculations of the Mean Force Potential. *Mol. Simul.* **1992**, *9*, 201–211. (e) Allen, M. P. and Tildesley, D. J. *Computer Simulation of Liquids*. Oxford University Press: New York, **1987**.

Detailed analysis of the static DFT energy profile

The energy profile shown in Fig. 7 has been simplified for the sake of clear presentation. IRC analysis (Fig. S3) of the MCA + HMCA dimer deprotonation TS at +7.1 kcal/mol reveals an additional intermediate at +6.0 kcal/mol, before the product state. This agrees with the MD simulations that also indicate a stable state near the TS (Fig. 8b), which converts to the product state via thermal motion as committer analysis started from the TS ensemble yields a near 50-50 distribution of dimer and product configurations.

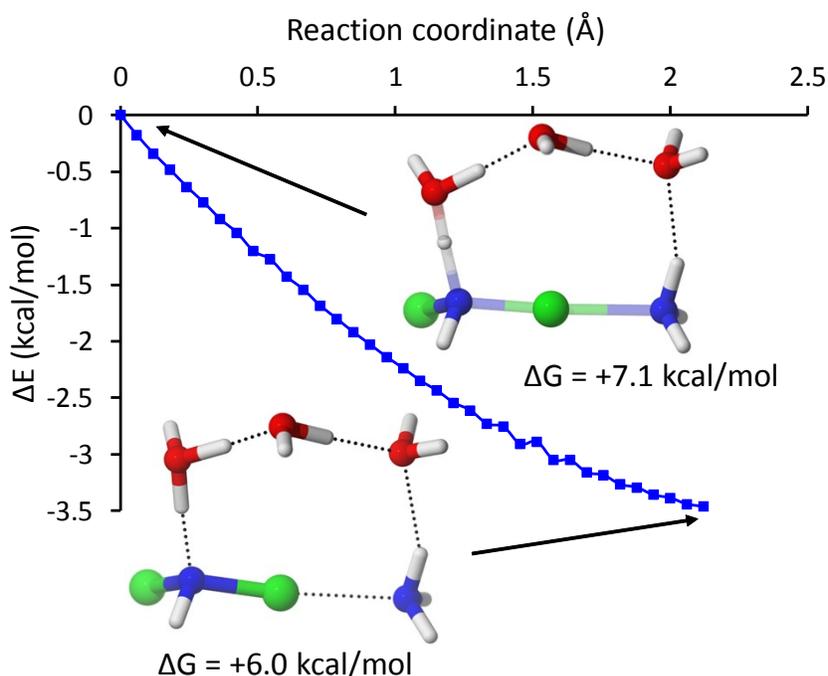


Figure S3. Product-side IRC profile of the MCA + HMCA dimer deprotonation. The ΔE on the vertical axis corresponds to electronic energy differences. The +6.0 kcal/mol free energy was obtained after optimizing the final point of the IRC.

From this intermediate a relaxed potential energy scan of a $\text{H}(\text{H}_2\text{O})\text{-N}(\text{NH}_3)$ bond distance was initiated, which indicated an essentially barrierless process for the conversion to the product state. The structure of the obtained product is shown in Fig. 7. However, after evaluating a few conformers, a slightly more stable configuration is obtained. In Fig. 7 this lower energy is shown. Both structures are included in the coordinates section.

Cartesian coordinates and energies of the static DFT structures

The .xyz format provided here can be directly read by the free Avogadro or Mercury software. The energy values are in atomic units while the coordinates are in Angstroms.

18
lprot_reactant, E(SCF) = -1261.14678149, E(ZPE) = -1261.444604, E(G) = -1261.491056 a.u.

N	-1.46380100	-0.37443400	-0.44330100
H	-1.00119300	0.54093400	-0.69081700
H	-2.51752900	-0.26288000	-0.39909500
H	-1.21949100	-1.08873300	-1.13433100
Cl	-0.89284500	-0.89167700	1.11951600
H	2.41090500	0.24070200	0.84920500
N	2.84470000	-0.62792200	0.51703400
H	2.46416000	-1.37180300	1.10004400
Cl	2.08942200	-0.89397100	-1.06464500
O	1.56364700	1.98089400	1.22324400
H	1.03345400	1.89660700	2.02309200
H	0.90986500	2.05329400	0.50586000
O	-0.22787800	1.99061200	-0.97362700
H	-0.83600200	2.73518800	-1.06634300
H	0.28296000	1.98033900	-1.79335200
O	-4.13443400	-0.04131500	-0.24969200
H	-4.56605600	-0.73580300	0.26316100
H	-4.57984700	-0.05684500	-1.10576500

18
lprot_reactant-dimer, E(SCF) = -1261.14517929, E(ZPE) = -1261.446738, E(G) = -1261.491399 a.u.

N	-1.76585300	-2.09386000	-0.18469300
H	-2.06596100	-2.48181900	-1.08063200
H	-2.45257800	-1.38800000	0.15976300
H	-1.66068800	-2.85094100	0.49258500
Cl	-0.15401500	-1.24613800	-0.39825000
H	1.58948700	0.92557300	-0.57387400
N	1.84903300	-0.07053100	-0.64160600
H	2.33849900	-0.23191400	-1.52076800
Cl	3.01117400	-0.35928400	0.63417500
O	0.83958400	2.58074800	-0.26449900
H	1.12037800	3.00369900	0.55425300
H	-0.12589700	2.45641800	-0.16336000
O	-1.91731700	2.30242800	-0.10885000
H	-2.38701900	1.49489400	0.16947300
H	-2.27842500	2.50362300	-0.97936000
O	-3.35741100	-0.00756800	0.71362800
H	-3.50935400	-0.01675000	1.66734200
H	-4.24124000	0.02327600	0.32571700

18

lprot_TS, E(SCF) = -1261.12300788, E(ZPE) = -1261.437774, E(G) = -1261.479690 a.u.

N	-1.64260000	-2.47233200	-0.15757300
H	-1.88215300	-2.92016800	-1.03627100
H	-2.38907100	-1.83794600	0.12086700
H	-1.51279400	-3.18439600	0.55408800
Cl	0.18881800	-1.11804700	-0.36217800
H	1.07619800	1.34962600	-0.34100200
N	1.59471800	0.11348000	-0.54059100
H	1.97460000	-0.04717300	-1.47611800
Cl	2.91962300	-0.21613900	0.55902900
O	0.58913800	2.37292700	-0.20807800
H	0.89466000	2.77850000	0.61589100
H	-0.42497100	2.29481800	-0.15856300
O	-1.96714700	2.25709400	-0.14994400
H	-2.42095500	1.43311800	0.12802800
H	-2.31686000	2.45395600	-1.02691500
O	-3.34500600	-0.02244300	0.64443100
H	-3.48941400	-0.01292000	1.59855600
H	-4.23343100	0.02508900	0.27084800

18

lprot_TS_IRC-intermediate, E(SCF) = -1261.12943960, E(ZPE) = -1261.437391, E(G) = -1261.481418 a.u.

N	-1.61179700	-2.73897600	-0.03938300
H	-1.89458500	-3.24923700	-0.87008800
H	-2.35486800	-2.08777000	0.19946900
H	-1.52281100	-3.40892600	0.71805500
Cl	0.32630600	-1.12794200	-0.33942900
H	0.83612100	1.59089800	-0.18422100
N	1.55456500	0.17409800	-0.54914600
H	1.89816300	0.05090400	-1.50430000
Cl	2.98186200	-0.10577200	0.45102600
O	0.34257100	2.45250200	0.05049900
H	0.50494800	2.64093400	0.98737300
H	-0.71038300	2.32660700	-0.10048900
O	-2.07810200	2.24546700	-0.31860800
H	-2.50518100	1.41422900	-0.00234000
H	-2.27436000	2.30243000	-1.26191000
O	-3.29136700	-0.02157100	0.57802600
H	-3.41139600	0.00397400	1.53512800
H	-4.18870100	-0.06794600	0.22653900

18

lprot_product, E(SCF) = -1261.16673400, E(ZPE) = -1261.465337, E(G) = -1261.509354 a.u.

N	3.19762000	-0.20701800	0.35749400
H	3.09381700	-0.03333200	1.35740600
H	4.17628900	-0.08107000	0.09889200
H	2.92337400	-1.16912300	0.15827700
Cl	-0.27902200	-0.93909400	1.54015700
H	-2.28606900	0.41450200	-0.19027200
N	-1.28127700	-1.19783700	0.10730400
H	-1.73412700	-2.09592000	0.29746300

Cl	-0.28433900	-1.53615100	-1.31162400
O	-2.64111000	1.32126200	-0.22376100
H	-2.91754800	1.44339400	-1.13902200
H	-1.17243500	2.25792200	0.22359000
O	-0.33446100	2.71557700	0.44234500
H	0.93183600	1.97802500	-0.53519700
H	-0.18945200	2.51991100	1.37481500
O	1.66429600	1.59372700	-1.06634000
H	2.59582600	0.45917900	-0.18388100
H	1.23142300	1.17513300	-1.81866700

18

1prot_product_conf2, E(SCF) = -1261.16700156, E(ZPE) = -1261.465598, E(G)
= -1261.510296 a.u.

N	2.02199800	1.99104300	0.40051400
H	1.95045800	1.37949300	-0.44651600
H	3.00332100	2.16392000	0.61923800
H	1.55656800	2.88268200	0.23336400
Cl	-1.69576400	-1.30392500	-0.56633100
H	0.00556300	-0.44339800	1.69423800
N	-1.55364500	-0.01210200	0.63009100
H	-2.46574600	-0.01951200	1.09504800
Cl	-1.51248900	1.57213900	-0.15097300
O	0.77647600	-0.90309100	2.07256300
H	1.19281300	-0.26395100	2.66135900
H	1.62489600	-1.63383100	0.65982400
O	2.04181800	-1.96883600	-0.15944500
H	1.89274400	-0.60295200	-1.27153500
H	1.49172700	-2.71392900	-0.42570900
O	1.79346300	0.25106100	-1.74680100
H	1.58277600	1.52508000	1.19493800
H	2.53264100	0.28107600	-2.36485600

19

2prot_reactant, E(SCF) = -1261.58373124, E(ZPE) = -1261.867520, E(G) = -
1261.908827 a.u.

N	-1.99398800	-1.32602100	-0.18427200
H	-1.93621200	-0.63948800	0.63294400
H	-1.57049800	-2.22459600	0.07075400
H	-2.97613000	-1.48144900	-0.43399400
Cl	-1.15513900	-0.66741100	-1.56281300
H	3.44203000	-0.51309500	0.00326900
N	2.45283600	-0.56328400	-0.25896600
H	2.33980300	-1.26869500	-0.99304600
Cl	1.52722100	-1.05087500	1.13647500
O	1.59762300	1.76521800	-1.02925800
H	2.09412100	0.41312500	-0.60299800
H	1.38190700	1.76339800	-1.96979600
O	-0.65513100	2.53092200	0.24038700
H	-1.04791100	1.87186200	0.84023600
H	-0.54291300	3.32321200	0.77729300
O	-1.86165500	0.48131400	1.78035900
H	-1.39632300	0.18963400	2.57565900
H	-2.74097100	0.74227700	2.08477700

H 0.76907300 2.04017800 -0.56658500

19

2prot_dimer, E(SCF) = -1261.57688647, E(ZPE) = -1261.864076, E(G) = -1261.906066 a.u.

N	2.12740600	-1.87533500	0.07550700
H	2.64558700	-1.00840300	-0.15218500
H	2.16340000	-2.53164900	-0.70701800
H	2.51681700	-2.31675700	0.91107800
Cl	0.39745100	-1.37836400	0.38329100
H	-1.64972800	0.41211000	1.05154200
N	-1.77754900	-0.53740100	0.69015200
H	-2.40995100	-1.04367600	1.30865500
Cl	-2.60459900	-0.36659500	-0.84273700
O	-0.69198200	2.16701700	1.22567900
H	-0.18277600	2.15267100	2.04698500
H	-1.20247800	2.98682300	1.25980400
O	0.75486700	2.08414700	-0.85003500
H	1.62823600	1.58856200	-0.68490300
H	0.24918200	1.60061700	-1.52160900
O	2.95484100	0.80955600	-0.41649300
H	3.59560500	0.95216400	-1.12668900
H	3.38495000	1.15331900	0.37869600
H	0.19187500	2.12191000	0.01340800

19

2prot_TS, E(SCF) = -1261.55194769, E(ZPE) = -1261.846648, E(G) = -1261.887779 a.u.

N	2.20937300	-2.34770500	-0.40665700
H	1.81033500	-2.53939000	-1.32233400
H	1.90940000	-3.09918400	0.20961900
H	3.21592700	-2.46392000	-0.51302000
Cl	-0.10626100	-0.99277200	0.24013300
H	-1.28265000	1.00018100	0.41524200
N	-1.54829300	-0.04663400	0.60581700
H	-1.78306100	-0.18949800	1.59712900
Cl	-2.94900800	-0.47253100	-0.34433200
O	-0.70029500	2.34987000	0.08348400
H	-0.85826500	2.97617100	0.80513000
H	-1.16337100	2.72093900	-0.68226400
O	1.97863800	2.18968100	-0.47831400
H	2.43724600	1.21133400	-0.05860200
H	2.09152700	2.22479200	-1.43915300
O	3.01003400	0.20939100	0.41149800
H	3.00379000	0.24310300	1.37762600
H	2.61278900	-0.66353300	0.14950500
H	1.01133800	2.25800400	-0.29497000

19

2prot_product, E(SCF) = -1261.60139013, E(ZPE) = -1261.887074, E(G) = -1261.930371 a.u.

N	2.47477700	-1.48124200	0.89516100
H	2.04014400	-2.29219700	0.45445000
H	1.74719000	-0.88014800	1.31192700

H	3.12058000	-1.79943200	1.61723700
Cl	-1.10048300	-1.30224200	-0.91784100
H	-0.40942700	0.17323500	1.44846600
N	-1.85026900	-0.48913700	0.46092200
H	-2.51108100	-1.18373400	0.81934500
Cl	-2.88672800	0.83646300	-0.06907100
O	0.50072200	0.47947600	1.64478500
H	0.45586800	0.97243000	2.47367200
H	1.01484100	1.26428900	0.46827000
O	1.37300800	1.70438600	-0.39126300
H	3.62753700	0.29428900	-1.94041500
H	2.25542900	1.26239700	-0.65239400
O	3.52886100	0.47262700	-0.99581400
H	4.33777700	0.93319900	-0.73597100
H	2.98257100	-0.93275500	0.18644000
H	1.52887800	2.64741500	-0.22776000