

# ORCA Lab 3

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## Method and Results

For all reactants, products and transition states, the method and basis used for geometry optimization has been B3LYP/Def2-SVP. In addition the optimized geometry for the stationary states, as well as the transition state, have also been calculated using the more accurate B3LYP/Def2-TZVPD method and basis.

An initial calculation of and geometry optimization was carried out for  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_3\text{Br}$ . The optimized geometries for these systems were then used as an initial guess for optimizations of the  $\text{CH}_3\text{Cl}\cdots\text{Br}^-$  and  $\text{Cl}^-\cdots\text{CH}_3\text{Br}$  complexes. The Mulliken charges of these systems were also investigated and are presented in tables 1 and 2.

The solvation model used was the *conductor-like polarizable continuum model* (CPCM) of dimethylformamide (DMF). This is a very approximate approximation of the solvent where the solvent is assumed to be a dielectric polarizable continuum. This continuum extends up to a distance from the solute, creating a cavity in the solvent where the solute is placed. The cavity thus has the approximate shape of the solute. What it lacks in accuracy it makes up for in computational speed.[1]

Table 1: Mulliken charges, calculated for optimal geometries using Def2-SVP basis.

	$Q_{\text{C}}$	$Q_{\text{Cl}}$	$Q_{\text{Br}}$
$\text{CH}_3\text{Cl} + \text{Br}^-$	-0.007	-0.189	-1.000
$\text{Cl}^- + \text{CH}_3\text{Br}$	-0.061	-1.000	-0.159
$\text{CH}_3\text{Cl}\cdots\text{Br}$	0.041	-0.306	-0.890
$\text{Cl}^-\cdots\text{CH}_3\text{Br}$	0.022	-0.788	-0.375
$[\text{Cl}\cdots\text{CH}_3\cdots\text{Br}]^-$	0.036	-0.652	-0.576

Table 2: Mulliken charges, calculated for optimal geometries using Def2-TZVPD basis.

	$Q_{\text{C}}$	$Q_{\text{Cl}}$	$Q_{\text{Br}}$
$\text{CH}_3\text{Cl} + \text{Br}^-$	-0.488	-0.195	-1.000
$\text{Cl}^- + \text{CH}_3\text{Br}$	-0.522	-1.000	-0.156
$\text{CH}_3\text{Cl}\cdots\text{Br}$	-0.547	-0.319	-0.934
$\text{Cl}^-\cdots\text{CH}_3\text{Br}$	-0.559	-0.858	-0.400
$[\text{Cl}\cdots\text{CH}_3\cdots\text{Br}]^-$	-0.583	-0.701	-0.590

A sweep of the Cl–C distance was carried out in order to identify a transition state along that reaction coordinate, and the transition state was found at a distance of 2.5 Å with a complex frequency of  $-282.42\text{ cm}^{-1}$ .

Finally, the reaction was calculated under the influence of a solvation model. The solvent being modelled was dimethylformamide (DMF). The Gibbs free energy,  $G$ , was calculated for all

stationary states as well as for the transition state. The values for these can be found in figure 1.

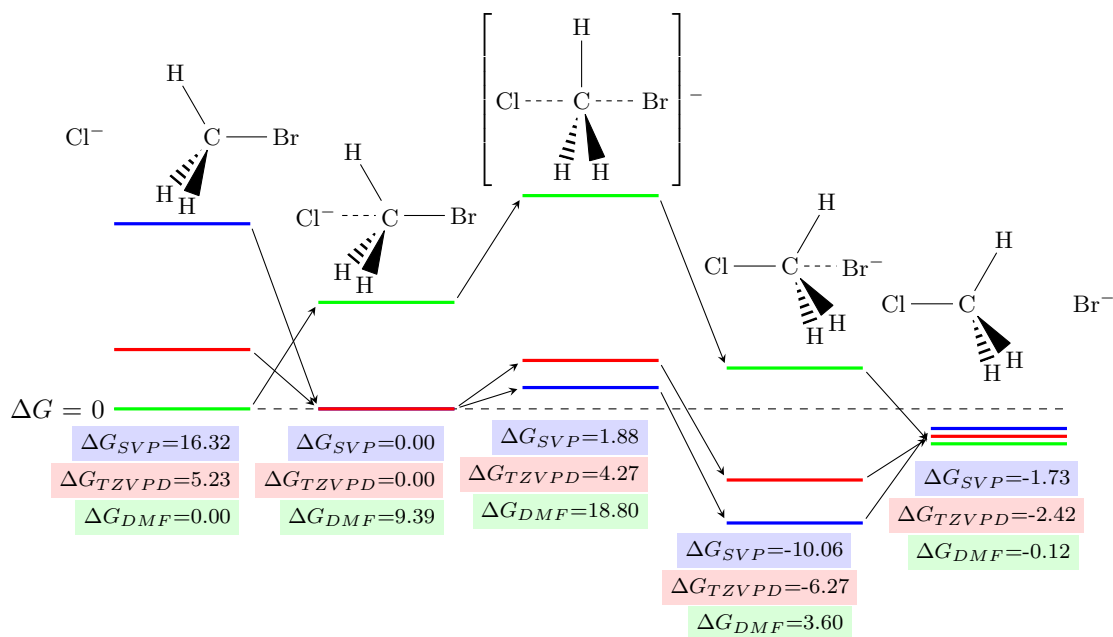


Figure 1: Reaction diagram for the three methods studied: B3LYP/Def2-SVP (blue), B3LYP/Def2-TZVPD (red), B3LYP/Def2-TZVPD with CPCM(DMF) (green). All units in kcal/mol.

I also calculated the reaction rate that is predicted by transition state theory, i.e. the rate over the largest barrier, using the Eyring equation. From this I see that I get a value of  $k = 0.0904 \text{ s}^{-1}$  for the reaction barrier value of  $\Delta G = 18.80 \text{ kcal/mol}$ .

## Discussion

From the results presented in this report, we can see that there are several things worth discussing further. Starting with the Mulliken charges that we have calculated, we can see that the molecule is quite polar, with even more charge being transferred to the more electronegative side as we form the complexes. That is, for both  $\text{CH}_3\text{Cl}\cdots\text{Br}$  and  $\text{Cl}^-\cdots\text{CH}_3\text{Br}$  we see that the more bound halide gains net charge as the other halide approaches. This can be due to the other halide screening the positive hydrogens as it approaches.

Our reaction diagram shows significant change in behavior as we add our solvation model. Both our gas phase calculations have a similar shape, where we have two "valleys" and three "peaks", while in gas phase we have exchanged our many small peaks for a single mountain.

According to transition state theory, the reaction should be limited by the largest barrier, in the gas phase calculation this would then be (using our bigger basis) the transition state barrier from our reactant complex, at 4.27 kcal/mol. We find that the same step is indeed the peak of our solvated reaction as well, although here we also have to go up hill in order to get to the reactant. In the solvation model we find that the reaction barrier is 18.80 kcal/mol, in close agreement with the experimental value of 17.7 kcal/mol, just a fraction of a kcal away from being able to claim chemical accuracy (1 kcal/mol).

Of the bat one would have assumed that this aprotic solvent would favor the  $\text{S}_{\text{N}}2$  reaction, but since it seems like the opposite is true here I would argue that this comes from the fact that we are comparing to a gas phase reaction. Even though aprotic, DMS will probably screen our anions to some extent.

We also see the importance of having a large enough basis, as our two first energy levels get a relative shift of 11 kcal/mol when using the bigger Def2-TZVPD basis.

## Conclusion

We predict the gas-phase transition state barrier to be 4.27 kcal/mol, while we get a calculated value of 18.80 kcal/mol for the reaction in a solution of DMF. This is still quite far from the experimental value.

We also see the importance of the size of the basis set that is used. We also see that the use of a solvent as compared to the gas-phase reaction only hinders the reaction, and increases the height of the transition state barrier.

## References

- [1] *Continuum solvation (CPCM, COSMO, SMD)*. URL: <https://sites.google.com/site/orcainputlibrary/continuum-solvation> (visited on 11/30/2020).

## A Extra tables

Table 3: Single point energy ( $E_{SP}$ ), enthalpy ( $H$ ), Gibbs free energy ( $G$ ), and the Gibbs free energy minus the electron energy ( $G - E_{el}$ ). We do not calculate the enthalpy for single point calculations with the Def2-TZVPD basis.

		$E_{SP}$	$H$	$G$	$G - E_{el}$
Def2-SVP	$\text{Br}^-$	-1615073.63	-1615070.37	-1615082.01	-8.38
	$\text{CH}_3\text{Br}$	-1640045.72	-1640020.05	-1640038.23	7.48
	$\text{CH}_3\text{Cl}$	-313659.67	-313633.71	-313651.07	8.60
	$\text{CH}_3\text{Cl} + \text{Br}^-$	-1928733.30	-1928704.08	-1928733.08	0.22
	$\text{CH}_3\text{Cl}\cdots\text{Br}^-$	-288669.14	-288665.88	-288676.80	-7.66
	$\text{Cl}^-$	-1928714.85	-1928685.93	-1928715.03	-0.18
	$\text{Cl}^- + \text{CH}_3\text{Br}$	-1928745.93	-1928718.45	-1928741.40	4.52
	$\text{Cl}-\cdots\text{CH}_3\text{Br}$	-1928735.41	-1928708.47	-1928731.35	4.06
	$[\text{Cl}\cdots\text{CH}_3\cdots\text{Br}]^-$	-1928733.65	-1928707.44	-1928729.47	4.18
Def2-TZVPD	$\text{Br}^-$	-1615290.44	-	-1615282.06	-
	$\text{CH}_3\text{Br}$	-1640273.67	-	-1640281.15	-
	$\text{CH}_3\text{Cl}$	-313792.68	-	-313801.28	-
	$\text{CH}_3\text{Cl} + \text{Br}^-$	-1929083.12	-	-1929083.34	-
	$\text{CH}_3\text{Cl}\cdots\text{Br}^-$	-1929091.27	-	-1929095.79	-
	$\text{Cl}^-$	-288801.39	-	-288793.73	-
	$\text{Cl}^- + \text{CH}_3\text{Br}$	-1929075.06	-	-1929074.88	-
	$\text{Cl}-\cdots\text{CH}_3\text{Br}$	-1929084.54	-	-1929088.60	-
	$[\text{Cl}\cdots\text{CH}_3\cdots\text{Br}]^-$	-1929080.39	-	-1929084.57	-
Def2-TZVPD DMF	$\text{Br}^-$	-1615355.95	-	-1615347.57	-
	$\text{CH}_3\text{Br}$	-1640276.30	-	-1640283.78	-
	$\text{CH}_3\text{Cl}$	-313795.35	-	-313803.95	-
	$\text{CH}_3\text{Cl} + \text{Br}^-$	-1929151.30	-	-1929151.52	-
	$\text{CH}_3\text{Cl}\cdots\text{Br}^-$	-1929148.93	-	-1929153.46	-
	$\text{Cl}^-$	-288871.52	-	-288863.86	-
	$\text{Cl}^- + \text{CH}_3\text{Br}$	-1929147.83	-	-1929147.65	-
	$\text{Cl}-\cdots\text{CH}_3\text{Br}$	-1929142.67	-	-1929146.73	-
	$[\text{Cl}\cdots\text{CH}_3\cdots\text{Br}]^-$	-1929133.38	-	-1929137.56	-