

# 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 table 1.

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

	$Q_{\text{C}}$	$Q_{\text{Cl}}$	$Q_{\text{Br}}$
$\text{CH}_3\text{Cl} + \text{Br}^-$	-0.488	-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	-0.858	-0.400
$\text{Cl}^-\cdots\text{CH}_3\text{Br}$	-0.559	-0.319	-0.934
$[\text{Cl}\cdots\text{CH}_3\cdots\text{Br}]^-$	-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 figures 1, 2, and 3.

1 is not to scale, while 3a and 3b are.

We also calculate the reaction rate predicted that one would get if we would see this energy barrier in experiments from the Eyring equation. From this we see that we get a value of  $k = 261130.42$ .

## 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 diagrams show that we will expect a potential energy barrier along our reaction coordinate that is around 5 kcal/mol in gas phase, and predicted to be 10 kcal/mol in solution which can be compared to the experimental value of 17.7 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

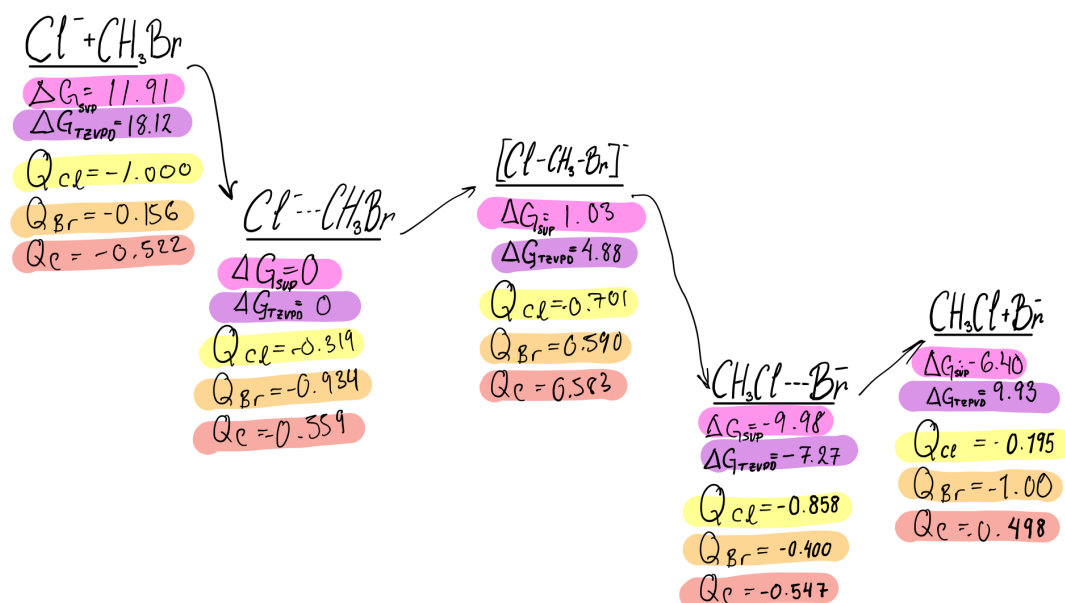


Figure 1: A handmade reaction diagram, even color coded for maximum flair. The diagram is drawn with the Def2-SVP basis in mind. Mulliken charges are written out for the halides and the carbon in each state.

opposite is true here I would argue that this comes from the fact that we are comparing to a gas phase reaction. Even though apotic, DMS will probably screen our anions to some extent.

We also see the importance of having a large enough basis, as our barrier shifts almost 4 kcal/mol when using the bigger Def2-TZVPD basis.

Finally, if we look at the reaction rate we calculate with our value versus the value calculated from the experimental transition state barrier of 17.7 kcal/mol, we see that we overestimate the reactivity by at least five orders of magnitude ( $10^5$ ).

A good reference is the value for "chemical accuracy" which is about 1 kcal/mol. Although a 1 kcal/mol error from the experimental value in this case still results in roughly a five fold increase or decrease of the reactivity.

## Conclusion

We predict the gas-phase transition state barrier to be 4.88 kcal/mol, while we get a calculated value of 10.02 kcal/mol for the reaction in a solution of DMF. This is still quite far from the

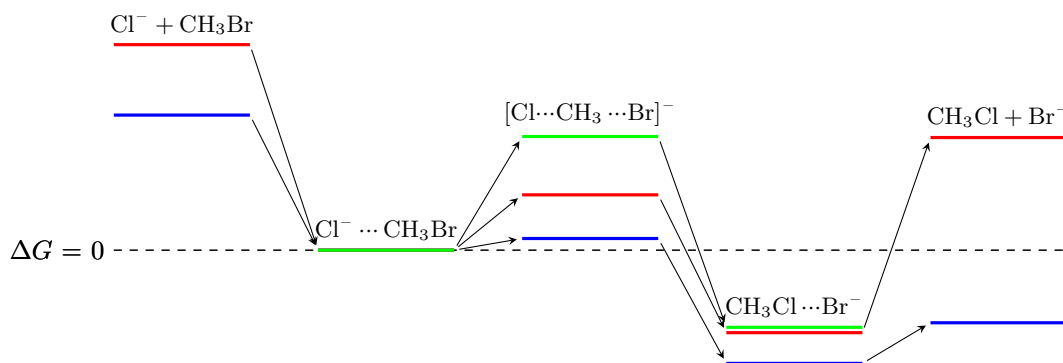


Figure 2: Reaction diagram when using B3LYP/Def2-TZVPD.

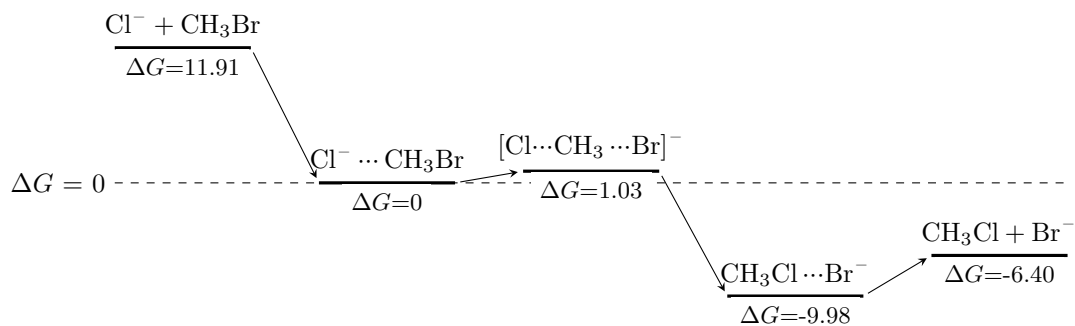
experimental value.

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.

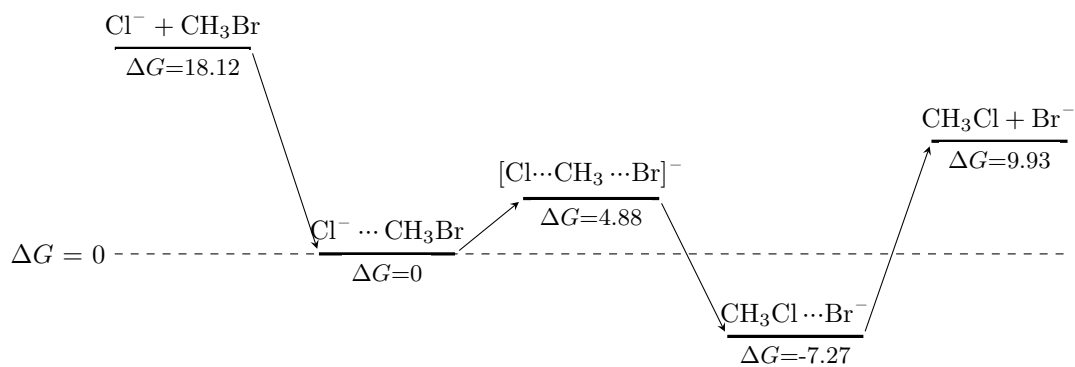
## A Extra tables

Table 2: 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.

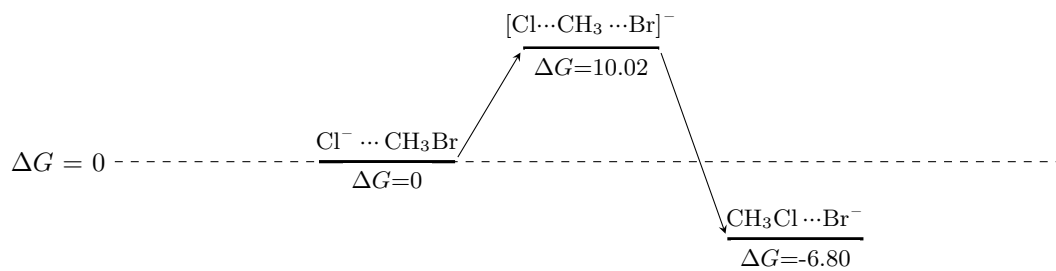
		$E_{SP}$	$H$	$G$	$G - E_{el}$
Def2-SVP	$\text{Br}^-$	-1615073.63	-1615070.37	-1615082.01	-8.38
	$\text{CH}_3\text{Br}$	-1640045.72	-1640020.05	-1640031.85	13.87
	$\text{CH}_3\text{Cl}$	-313659.67	-313633.71	-313644.94	14.73
	$\text{CH}_3\text{Cl} + \text{Br}^-$	-1928733.30	-1928704.08	-1928726.95	6.34
	$\text{Cl}^-$	-288669.14	-288665.88	-288676.80	-7.66
	$\text{Cl}^- + \text{CH}_3\text{Br}$	-1928714.85	-1928685.93	-1928708.64	6.21
	$\text{CH}_3\text{Cl}\cdots\text{Br}^-$	-1928745.93	-1928718.45	-1928730.53	15.40
	$\text{Cl}\cdots\text{CH}_3\text{Br}$	-1928735.41	-1928708.47	-1928720.55	14.86
	$[\text{Cl}\cdots\text{CH}_3\cdots\text{Br}]^-$	-1928733.65	-1928707.44	-1928719.52	14.13
Def2-TZVPD	$\text{Br}^-$	-1615290.44	-	-1615282.06	-
	$\text{CH}_3\text{Br}$	-1640273.67	-	-1640287.54	-
	$\text{CH}_3\text{Cl}$	-313792.68	-	-313807.40	-
	$\text{CH}_3\text{Cl} + \text{Br}^-$	-1929083.12	-	-1929089.46	-
	$\text{CH}_3\text{Cl}\cdots\text{Br}^-$	-1929091.27	-	-1929106.67	-
	$\text{Cl}^-$	-288801.39	-	-288793.73	-
	$\text{Cl}^- + \text{CH}_3\text{Br}$	-1929075.06	-	-1929081.27	-
	$\text{Cl}\cdots\text{CH}_3\text{Br}$	-1929084.54	-	-1929099.39	-
	$[\text{Cl}\cdots\text{CH}_3\cdots\text{Br}]^-$	-1929080.39	-	-1929094.52	-
Def2-TZVPD DMF	$\text{CH}_3\text{Cl}\cdots\text{Br}^-$	-1929142.67	-	-1929158.07	-
	$\text{Cl}^- \cdots \text{CH}_3\text{Br}$	-1929148.93	-	-1929163.79	-
	$[\text{Cl}\cdots\text{CH}_3\cdots\text{Br}]^-$	-1929133.38	-	-1929147.51	-



(a) Reaction diagram when using B3LYP/Def2-SVP.



(b) Reaction diagram when using B3LYP/Def2-TZVPD.



(c) Reaction diagram when using B3LYP/Def2-TZVPD and DMF solvent model.

Figure 3: The three reaction diagrams discussed in this report.