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COMPARISON OF OBTAINING METHYL CHLORIDE FROM QUANTUM CHEMISTRY VS. CLASSICAL CHEMISTRY

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ABSTRACT

Methyl chloride (CH3Cl) is a chemical with high production volume and is used as an industrial solvent. Selective formation of CH3Cl is a crucial process, but it is quite challenging to achieve with high selectivity due to a radical reaction. The objective of this research was to compare the methodology of quantum chemistry vs. classical chemistry. The purpose is to strengthen the theoretical calculations of obtaining CH3Cl to facilitate synthesis in laboratories and industry. The first thing we did was to propose a working hypothesis: "The synthesis reaction of CH3Cl in a natural way is reversible". Hyperchem software was used with the parametric semi-empirical quantum method 3 (SE-PM3). As a result: Reagents have a high probability of reacting because the interaction between them falls in a high probability zone. That is, they go to the bottom of the general quantum well. In conclusion, it has been found that the most likely reaction is that hydrochloric acid oxidizes to methanol, which has an Electron Transfer Coefficient (ETC) of 45.46. The direction of reaction from left to right. The catalyst's use is justified because the sum of ETCs of the reagents is less than the sum of the ETCs of the products.

INTRODUCTION

Methyl chloride (CH_3Cl; chloromethane) is a chemical with high production volume (> 1000t / y) and is used as an industrial solvent. Due to this high production, many scientists study the damage that can be caused by their manufacturing and marketing wastes to the environment and human beings [1-3].

The synthesis of this compound has been studied for many years and by different methods [2, 4-5]. Selective formation of CH_3Cl chloride is a crucial process, but it is quite challenging to achieve with high selectivity due to a radical reaction [6].

On the other hand, quantum chemistry is a tool that is currently used. In at least one investigation into the synthesis of CH_3Cl, calculations of Density Functional Theory (DFT) revealed that the surface of sulfated tin oxide could activate more Cl_2 molecules in a heterolytic manner. This activation leads to better catalytic yields compared to SnO_2 and sulfated zirconia catalysts. High-level quantum chemistry calculations predict energy barriers according to experimental observations, and the difference in nucleophilicity between O_3 and O_2. All these data are analyzed in the light of quantum chemistry calculations and Marcus theory [6, 7].

The objective of this research was to compare the methodology of quantum chemistry vs. classical chemistry. The purpose is to strengthen the theoretical calculations of obtaining CH_3Cl to facilitate synthesis in laboratories and industry.

MATERIALS AND METHODS

The first thing we did was to propose a working hypothesis:

"The synthesis reaction of chloromethane in a natural way is reversible."

This hypothesis has two corollaries:

The dichloromethane synthesis reaction is carried out more easily from left to right.

The dichloromethane synthesis reaction is carried out more easily from right to left.

Hyperchem software was used with the parametric semi-empirical quantum method 3 (SE-PM3). The adjustments and the parameterization of this simulator were made according to the theory of electron transfer coefficient (ETC) that has been published in other articles (see references) [8-20].

RESULTS AND DISCUSSION

Concerning our general hypothesis, we announce equation number one:

$$CH_3OH + HCl \leftrightarrow CH_3Cl + H_2O \qquad \textit{Equation. 1}$$

Equation 1 represents the chlorination reaction of methanol with hydrochloric acid from left to right, from right to left, represent the hydration of methyl chloride.

It is intended to determine the direction of the reaction by the principle of minimum action of Feynmann.

Table 1 shows the ETCs of all the substances involved in this reaction. This table shows that methanol has a lower ETC for all other substances. This value of methanol ETC, tells us that it is the most stable substance of all. CH_3Cl has a higher ETC of all substances. This value of CH_3Cl ETC means that it is the least stable substance of all. With these observations, the reaction is complicated.

The sum of the ETCs of the reagents is 120.857, while the sum of the reagents is 142.854. For this reason, it can be said that this reaction goes from a stable system to an unstable one. This reaction needs energy to be carried out in the direction from left to right. In the opposite direction, it should not need energy.

Table 1. ETCs of pure substances

No.	Reducing Agent	Oxidizing Agent	HOMO	LUMO	BG	E-	E	EP	ETC
1	CH_3Cl	CH_3Cl	-10.477	1.328	11.805	-0.023	0.111	0.134	88.098
2	HCl	HCl	-11.060	1.543	12.603	-0.023	0.164	0.187	67.398
3	H_2O	H_2O	-12.316	4.056	16.372	-0.127	0.172	0.299	54.756
4	CH_3OH	CH_3OH	-11.139	3.509	14.648	-0.115	0.159	0.274	53.459

Calculations of all possible interactions of the four substances involved in the reaction were made, and Table 2 was obtained.

Table 2. ETCs cross-band

No.	Reducing Agent	Oxidizing Agent	Homo	Lumo	BG	E-	E	EP	ETC
1	*HCl	**CH_3Cl	-11.060	1.328	12.388	-0.023	0.111	0.134	92.450
2	**CH_3Cl	**CH_3Cl	-10.477	1.328	11.805	-0.023	0.111	0.134	88.098
3	*HCl	*CH_3OH	-11.060	3.509	14.569	-0.023	0.159	0.182	80.050
4	*HCl	**H_2O	-11.060	4.056	15.116	-0.023	0.172	0.195	77.518
5	**CH_3Cl	*CH_3OH	-10.477	3.509	13.986	-0.023	0.159	0.182	76.846
6	**CH_3Cl	**H_2O	-10.477	4.056	14.533	-0.023	0.172	0.195	74.527
7	*HCl	*HCl	-11.060	1.543	12.603	-0.023	0.164	0.187	67.398
8	**CH_3Cl	*HCl	-10.477	1.543	12.020	-0.023	0.164	0.187	64.280
9	**H_2O	**CH_3Cl	-12.316	1.328	13.644	-0.127	0.111	0.238	57.330
10	**H_2O	*CH_3OH	-12.316	3.509	15.825	-0.127	0.159	0.286	55.333
11	**H_2O	**H_2O	-12.316	4.056	16.372	-0.127	0.172	0.299	54.756
12	*CH_3OH	*CH_3OH	-11.139	3.509	14.648	-0.115	0.159	0.274	53.459
13	*CH_3OH	**H_2O	-11.139	4.056	15.195	-0.115	0.172	0.287	52.943
14	*CH_3OH	**CH_3Cl	-11.139	1.328	12.467	-0.115	0.134	0.249	50.068
15	**H_2O	*HCl	-12.316	1.543	13.860	-0.127	0.164	0.291	47.628
16	*CH_3OH	*HCl	-11.139	1.543	12.682	-0.115	0.164	0.279	45.456

*From left to right: * Reative, ** Product. From right to left vice versa.*

Table 3 summarizes the most important observations. Note that the reaction is favored from left to right. This sense is due to the lower ETC of the reagents on the left that are at the bottom of the general quantum well interaction number 16.

Table 3. Observations in the most important interactions:

No.	Reducing Agent	Oxidizing Agent	ETC	Observations:
1	*HCl	**CH_3Cl	92.450	Unlikely interaction
2	**CH_3Cl	**CH_3Cl	88.098	Unlikely interaction
3	*HCl	*CH_3OH	80.050	Unlikely interaction
4	*HCl	**H_2O	77.518	Unlikely interaction
5	**CH_3Cl	*CH_3OH	76.846	Unlikely interaction
6	**CH_3Cl	**H_2O	74.527	Unlikely interaction
7	*HCl	*HCl	67.398	Unlikely interaction
8	**CH_3Cl	*HCl	64.280	Unlikely interaction
9	**H_2O	**CH_3Cl	57.330	Unlikely interaction
10	**H_2O	*CH_3OH	55.333	Azeotrope
11	**H_2O	**H_2O	54.756	Pure product or reagent. Form azeotrope with alcohol.
12	*CH_3OH	*CH_3OH	53.459	Pure product or reagent. Azeotrope form with water.
13	*CH_3OH	**H_2O	52.943	A reagent and a product. They form azeotropes. You have to distill.
14	*CH_3OH	**CH_3Cl	50.068	A reagent and a product. The product tends to be contaminated by the reagent. We must look for an excellent method of separation.
15	**H_2O	*HCl	47.628	A reagent and a product. The product tends to become contaminated with the reagent. The advantage is that HCl is very soluble and can be removed with water. The HCl reagent can be excess in the reaction from left to right. In this way, the reaction is accelerated by the principle of Chatelier.
16	*CH_3OH	*HCl	45.456	As reagent, they tend to react. The reaction is favored from left to right.

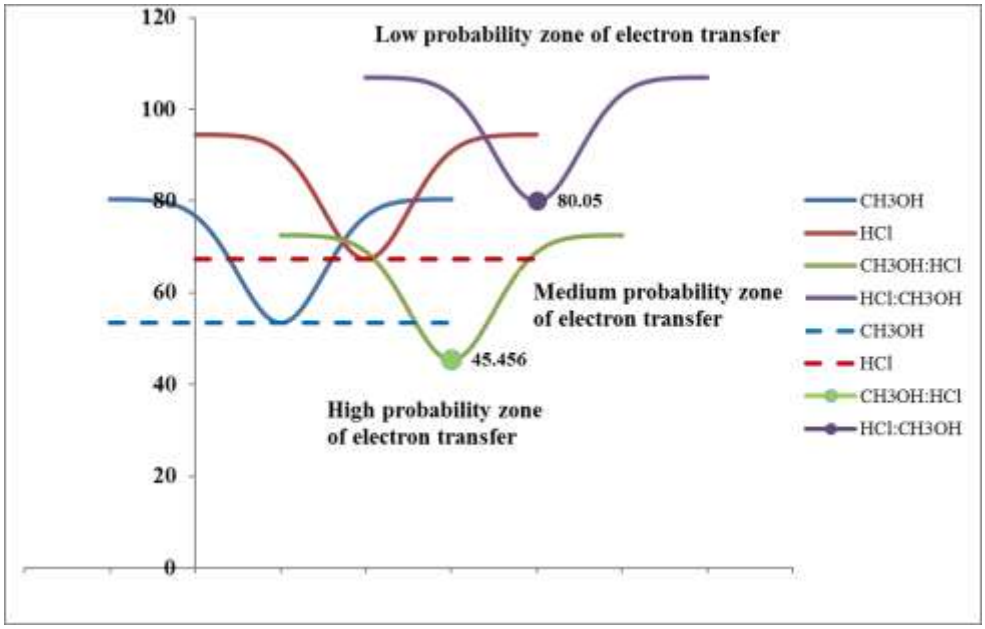

Figure 1. Quantum wells of reagents and their crossed bands. Reagents interact with high in high probability zone.

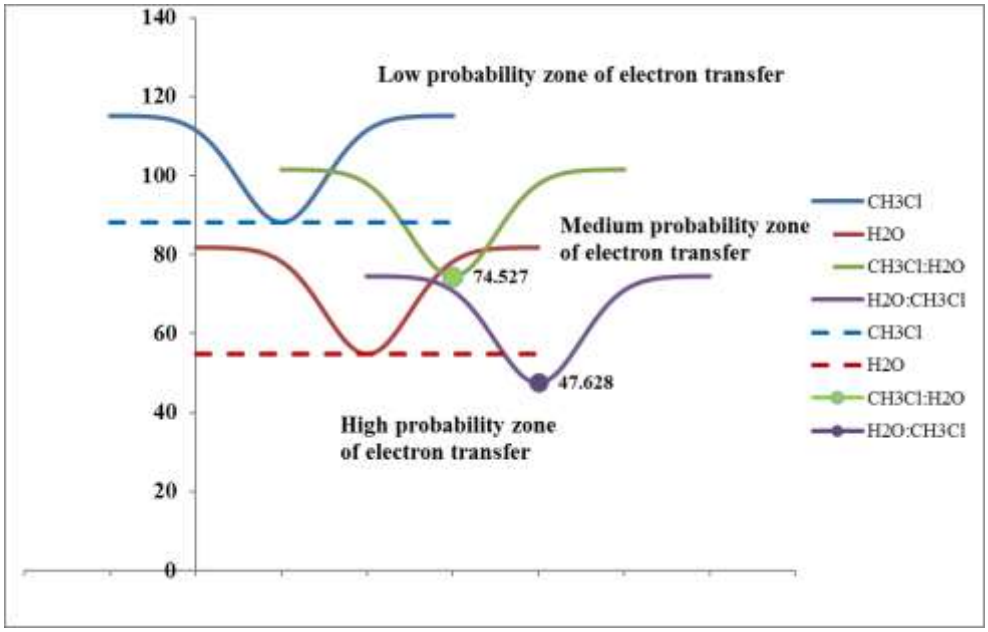

Figure 2. Quantum wells of the products and their crossed bands. The products interact in the high probability zone.

Figure 1 shows the quantum wells of the reagents. These reagents have a high probability of reacting because the interaction between them falls in a high probability zone; that is, they go to the bottom of the general quantum well.

In figure 2, the quantum wells of the products are shown. These products interact in a high probability zone. If the main product is methyl chloride, then it is contaminated with water. A drying or distillation is needed to purify it.

In general, the reaction from left to right is favored, and this reaction is unlikely to be reversible.

CONCLUSION

We compare quantum chemistry with classical chemistry and reach the following conclusions:

1. The SN_2 nucleophilic substitution reaction of methanol (as a reductant) with pure hydrochloric acid (as an oxidant) forms methyl chloride and water. The direction of reaction from left to right.
2. This reaction is most likely to occur because it has the lowest ETC (interaction 16, table 3).
3. According to classical chemistry, the hydroxyl group of methanol needs to be protonated to be an excellent leaving group.
4. This new structure can now react with the chloride ion and thus carry out the SN_2 nucleophilic substitution reaction.
5. In conclusion, it has been found that the most likely reaction is that hydrochloric acid oxidizes to methanol, which has an ETC of 45.46. The direction of reaction from left to right.
6. The catalyst's use is justified because the "ETCs sum" of the ETCs reagents is less than the sum of the "ETCs sum" of the products.

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