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# Reaction Paths for Aqueous Decomposition of CCl<sub>2</sub>

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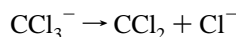
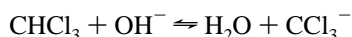
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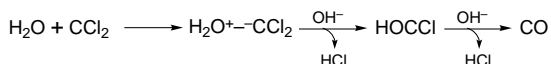
The potential energy surface (PES) for the H<sub>2</sub>O + CCl<sub>2</sub> reaction was investigated at the ab initio SCF and MP2 levels of theory, employing the DZP basis set, in order to determine the mechanism of basic aqueous decomposition of CCl<sub>2</sub>. Several possible pathways were considered, including reactions with other H<sub>2</sub>O molecules and OH<sup>−</sup>. We have found that the first step corresponds to insertion of CCl<sub>2</sub> into the O–H bond of water, resulting in the CHCl<sub>2</sub>OH species. This molecule loses HCl in one elimination reaction catalyzed by OH<sup>−</sup>, forming ClCHO. Again, OH<sup>−</sup> catalyzes the elimination of other HCl, resulting in CO, the decomposition product. The first step is the slow one, and we have used transition-state theory to estimate the rate constant for the aqueous decomposition of CCl<sub>2</sub>. The obtained rate constant was used for building a general picture of CHCl<sub>3</sub> decomposition in basic aqueous solution. The results of the present study are in agreement with experimental observations.

## Introduction

The CCl<sub>2</sub> is a very important reactive intermediate.<sup>1,2</sup> It can be generated in a mixture of chloroform and aqueous solution of sodium hydroxide. Hine<sup>3,4</sup> carried out kinetics experiments on basic hydrolysis of CHCl<sub>3</sub>, and concluded that the formation of CCl<sub>2</sub> proceeds according to the mechanism



Initially, a fast acid–base equilibrium between CHCl<sub>3</sub> and OH<sup>−</sup> occurs, followed by a slow loss of Cl<sup>−</sup> to form the CCl<sub>2</sub> species. Studies performed by Robinson<sup>5</sup> have shown that the CCl<sub>2</sub> reacts more preferentially with H<sub>2</sub>O than with OH<sup>−</sup>. It was proposed that CCl<sub>2</sub> forms an ylide species with H<sub>2</sub>O, and then 2 equiv of HCl are eliminated by action of OH<sup>−</sup> generating CO:



In a subsequent slower step, carbon monoxide reacts with OH<sup>−</sup>, resulting in HCOO<sup>−</sup>. However, the ylide intermediate was not experimentally detected, and in a recent ab initio study of the H<sub>2</sub>O⋯CCl<sub>2</sub> complex, we have shown that the supposed ylide does not exist,<sup>6</sup> although there is the formation of a H-bonded minimum energy structure with 2.5 kcal/mol of dissociation energy. So, another pathway should be proposed. In this work, we present a new mechanism for the aqueous decomposition of CCl<sub>2</sub> based on our ab initio calculations. In a first step, only H<sub>2</sub>O and CCl<sub>2</sub> are considered. In the second step, we analyzed the possibility of reactions with other H<sub>2</sub>O molecule and with the OH<sup>−</sup> ion.

## Details of Calculations

Otherwise stated, all geometries of minima and transition-state (TS) structures were fully optimized at the self-consistent-field (SCF) level using a double-ζ plus polarization function basis set (DZP).<sup>7</sup> The nature of the stationary points were

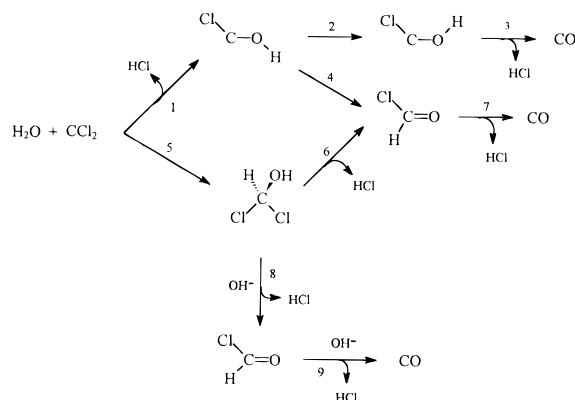


Figure 1. General scheme for decomposition of the CCl<sub>2</sub> species.

determined by harmonic frequency analysis. To take the electron correlation into account, we performed single-point calculations at the second-order Moller–Plesset perturbation theory level (MP2/DZP//SCF/DZP). Intrinsic reaction coordinate (IRC) calculations<sup>8</sup> were performed in order to establish the connection between reagents, transition states, and products. All calculations were performed with the GAMESS package.<sup>9</sup>

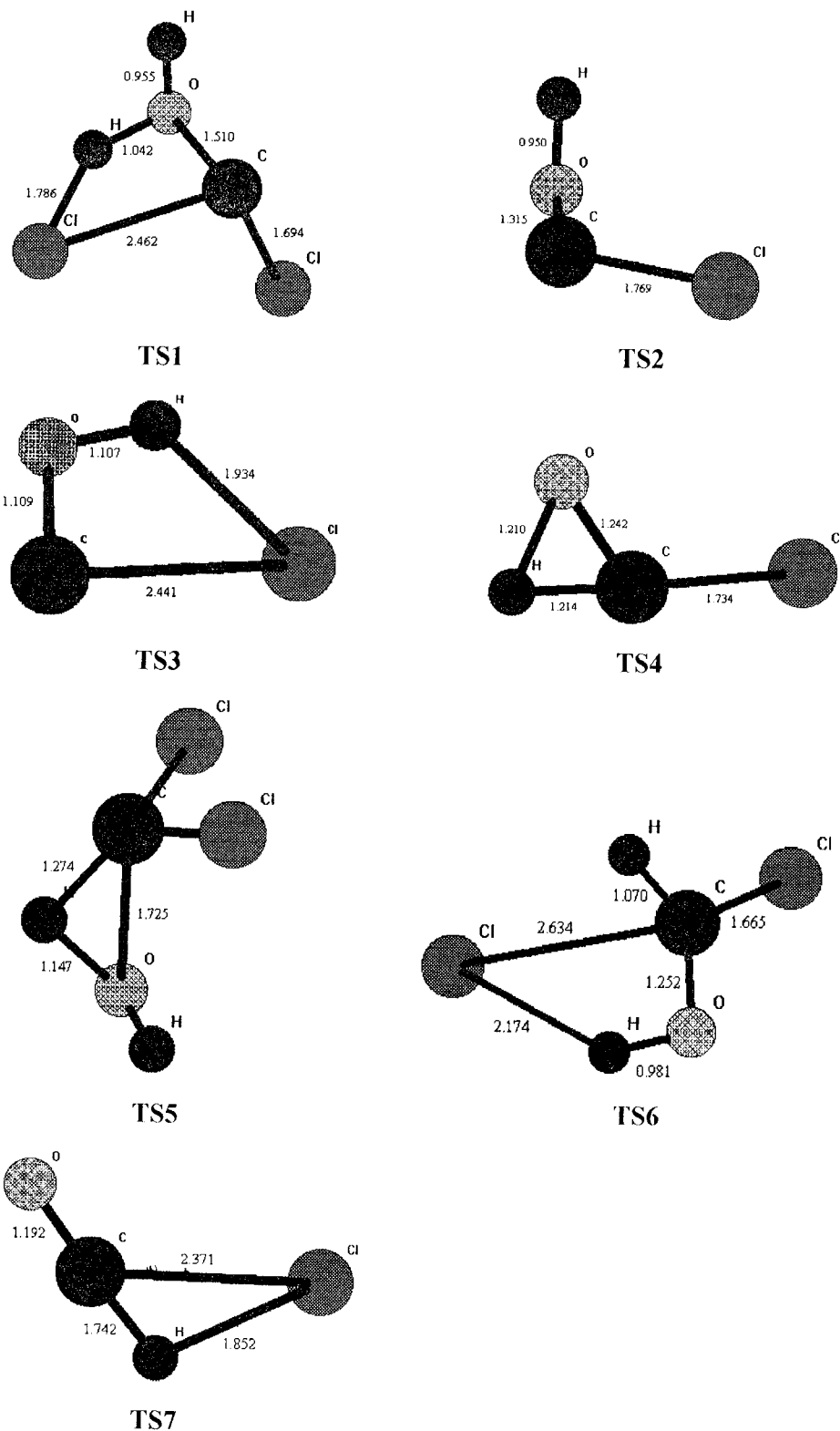
## Results and Discussion

### Overview of the Reactions and the Calculated Structures.

Several reaction paths were considered. Figure 1 presents a general scheme for the possible reactions, and the Figure 2 shows the transition states for reactions 1–7. The pathway through an ylide intermediate was not considered, once it was shown that this species does not form at SCF/DZP level of theory.<sup>6</sup> The first elementary step of the H<sub>2</sub>O + CCl<sub>2</sub> reaction can follow two routes. In reaction 1, an addition–elimination mechanism takes place, resulting in HCl and in chlorohydroxycarbene exhibiting a trans conformation. The *trans*-carbene formed can suffer isomerism to the *cis* form (reaction 2), which eliminates HCl by a unimolecular mechanism, resulting in the final CO product (reaction 3). Another possibility is the migration of the hydrogen atom bonded at the oxygen to carbon (reaction 4) that results in chloroformaldehyde.

The second possibility for the first step of the H<sub>2</sub>O + CCl<sub>2</sub> reaction is the insertion of CCl<sub>2</sub> in the O–H bond (reaction 5),

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**Figure 2.** Geometries of the first-order transition states for reactions 1–7 (see Figure 1). Reaction 1 corresponds to TS1, reaction 2 to TS2, and the others follow the same scheme.

resulting in dichloromethanol. This molecule can lose one HCl (reaction 6), forming chloroformaldehyde. Another unimolecular reaction (reaction 7) eliminates HCl, resulting in the CO product. The absolute energy, vibrational frequencies, and relative energies of minima and transition states structures are in Tables 1–3, respectively.

**Analysis of the Reaction Pathways.** Reaction 1 has a predicted activation energy of 30.43 kcal/mol, a relatively high value. The two subsequent possible pathways (reaction 2 and

4) have activation energies of 20.51 and 27.43 kcal/mol, respectively. A comparison of our results at higher levels taken from ref 10 show a very good agreement for reaction 4. The lower energy barrier for reaction 2 favors this process in relation to reaction 4. Reaction 3 has a barrier of 21.21 kcal/mol at the MP2/DZP//SCF/DZP level and 15.3 kcal/mol in MP4/6-311++G\*\*//MP2/6-311G\*\* level.<sup>10</sup> This disagreement is smaller for the reaction energy (−56.39 kcal/mol compared with −58.9 kcal/mol). The pathway following reaction 1 → 2 → 3

**TABLE 1: Absolute Energies of the Molecules and First-Order Transition-State Structures Connecting the Reagents and the Products Indicated**

species	SCF <sup>a</sup>	MP2 <sup>b</sup>
HCl	-460.057 538	-460.204 390
CO	-112.759 323	-113.035 773
H <sub>2</sub> O	-76.046 829	-76.241 471
CCl <sub>2</sub>	-956.703 418	-957.090 911
CICOH (cis)	-572.729 036	-573.157 077
CICOH (trans)	-572.731 225	-573.158 576
CICHO	-572.800 298	-573.240 217
CHCl <sub>2</sub> OH <sup>c</sup>	-1032.858 121	-1033.448 746
transition states		
H <sub>2</sub> O + CCl <sub>2</sub> → HCl + CICOH (trans)	-1032.694 286	-1033.285 850
CICOH (trans) → CICOH (cis)	-572.698 837	-573.123 064
CICOH (cis) → HCl + CO	-572.692 577	-573.118 066
CICOH (trans) → CICHO	-572.647 371	-573.109 042
H <sub>2</sub> O + CCl <sub>2</sub> → CHCl <sub>2</sub> OH	-1032.694 393	-1033.311 888
CHCl <sub>2</sub> OH → HCl + CICHO	-1032.793 837	-1033.375 693
CICHO → HCl + CO	-572.725 922	-573.161 381

<sup>a</sup> Ab initio SCF/DZP. <sup>b</sup> Ab initio MP2/DZP//SCF/DZP. <sup>c</sup> The most stable conformation  $\delta(\text{H}-\text{C}-\text{O}-\text{H}) = 180^\circ$ .

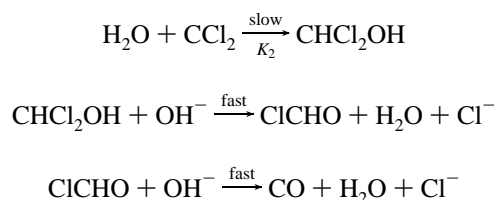
is not likely to take place. The high activation energy of reaction 1 would lead to a very low rate constant for decomposition of CCl<sub>2</sub>. In the experimental study reported by Robinson,<sup>5</sup> the disappearance of CHCl<sub>3</sub> is immediately followed by formation of CO, meaning that the slow step is the formation of CCl<sub>2</sub>, and the decomposition of this species is fast.

Reaction 5 is the second alternative for the initial step. Its activation energy is predicted to be 13.43 kcal/mol, considerably below the 30.43 kcal/mol value predicted for reaction 1. So, this should be the first step of the decomposition processes of CCl<sub>2</sub>. However, the subsequent steps, reactions 6 and 7 have a very high activation energy (44.42 and 46.72 kcal/mol). These two steps cannot be responsible for the decomposition reaction. Nevertheless, there is no doubt that the first step is reaction 5. So, we have to consider the influence of the other H<sub>2</sub>O molecules and of the OH<sup>-</sup> anion.

**Reactions with Other Environmental Species: H<sub>2</sub>O and OH<sup>-</sup>.** The possibility of OH<sup>-</sup> reacting initially with CCl<sub>2</sub> is discarded, once Robinson<sup>5</sup> showed that CCl<sub>2</sub> reacts preferentially with H<sub>2</sub>O. However, the CHCl<sub>2</sub>OH should be an acidic species,

due to the strong electron-withdrawing effect of Cl atoms. Indeed, in performing geometry optimizations for the CHCl<sub>2</sub>OH...OH<sup>-</sup> complex using a 6-31++G basis set, an immediate proton transfer from CHCl<sub>2</sub>OH to OH<sup>-</sup> takes place. The resulting anion CHCl<sub>2</sub>O<sup>-</sup> decomposes to Cl<sup>-</sup>...CICHO. No energy barrier exists for this process (reaction 8). The formed CICHO can suffer either hydration or acid-base reaction. The reaction of CICHO with H<sub>2</sub>O has an activation barrier of 43.6 kcal/mol,<sup>10</sup> a very high value. The acid-base reaction with OH<sup>-</sup> has no barrier in the gas phase, and the formed anion (CICO<sup>-</sup>) decomposes into the Cl<sup>-</sup>...CO complex (reaction 9). Again, no barrier occurs (at the SCF/6-31++G level). Another possibility is the nucleophilic attack of the OH<sup>-</sup> to the CICHO, resulting in the HCOO<sup>-</sup> species. This pathway is discarded, because in the reported experiments the formation of CO happen first and then this react with OH<sup>-</sup> to form HCOO<sup>-</sup>, as shown by Robinson.<sup>5</sup> We arrived at the following mechanism: First, a slow step occurs, resulting in CHCl<sub>2</sub>OH. Then the OH<sup>-</sup> present in the media catalyzes two fast subsequent HCl eliminations, generating CO, according to Scheme 1.

Scheme 1



The acid-base reaction with OH<sup>-</sup> was calculated in the gas phase. By the fact that ions are involved, the solvent should have an important effect in the reaction. The OH<sup>-</sup> is stabilized in solution, and so it is possible that an energy barrier exists in the acid-base reactions. However, these reactions types are in general very fast, and if any barrier exists, it should be low, and the rate-determining step of the decomposition of CCl<sub>2</sub> should correspond to process 5.

**Basic Hydrolysis of CHCl<sub>3</sub>.** We now show that our proposed mechanism is in accord with experimental kinetic measurements of basic hydrolysis of CHCl<sub>3</sub>. The rate of decomposition of CHCl<sub>3</sub> in NaOH solution forming the CCl<sub>2</sub>

**TABLE 2: Frequencies (in cm<sup>-1</sup>) and Zero-Point Energies (in kcal/mol) for the Molecules and the Transition States, Involved in the Reactions Indicated Below**

species	frequencies <sup>a</sup>	ZPE <sup>b</sup>
HCl	3152	4.06
CO	2428	3.12
H <sub>2</sub> O	1754, 4167, 4291	13.14
CCl <sub>2</sub>	368, 806, 870	2.63
CICOH (cis)	494, 701, 798, 1405, 1490, 3995	11.43
CICOH (trans)	499, 771, 782, 1408, 1466, 4107	11.62
CICHO	517, 838, 1070, 1481, 2029, 3322	11.91
CHCl <sub>2</sub> OH <sup>c</sup>	309, 346, 479, 498, 759, 861, 1263, 1375, 1390, 1547, 3434, 4131	21.09
transition states		
H <sub>2</sub> O + CCl <sub>2</sub> → HCl + CICOH (trans)	672i, 191, 339, 425, 454, 703, 851, 922, 1237, 1660, 2357, 4077	17.00
CICOH (trans) → CICOH (cis)	893i, 474, 753, 950, 1329, 4153	9.85
CICOH (cis) → HCl + CO	1158i, 367, 802, 932, 1831, 2407	8.16
CICOH (trans) → CICHO	2503i, 365, 497, 810, 1705, 2821	7.97
H <sub>2</sub> O + CCl <sub>2</sub> → CHCl <sub>2</sub> OH	1961i, 248, 293, 356, 472, 574, 801, 881, 1038, 1495, 2435, 4110	16.34
CHCl <sub>2</sub> OH → HCl + CICHO	233i, 276, 380, 488, 682, 866, 970, 1392, 1520, 1657, 3486, 3568	19.67
CICHO → HCl + CO	1174i, 272, 545, 944, 2298, 3062	9.16

<sup>a</sup> Frequencies obtained at the SCF/DZP level. <sup>b</sup> Zero-point energies, using the calculated frequencies scaled by 0.9 factor. <sup>c</sup> The most stable conformation  $\delta(\text{H}-\text{C}-\text{O}-\text{H}) = 180^\circ$ .

**TABLE 3. Reaction and Activation Energies for Several Reactions**

reaction	$\Delta E_{\text{SCF}}^a$	$\Delta E_{\text{MP2}}^b$	$\Delta \text{ZPE}^c$	$\Delta E_{\text{MP2}} + \Delta \text{ZPE}^d$	$\Delta E^e$
1 <sup>f</sup>	-24.17	-19.19	-0.09	-19.28	
1 <sup>g</sup>	35.12	29.2	1.23	30.43	
2 <sup>f</sup>	1.37	0.94	-0.19	0.75	
2 <sup>g</sup>	20.32	22.28	-1.77	20.51	
3 <sup>f</sup>	-55.11	-52.14	-4.25	-56.39	-58.9
3 <sup>g</sup>	22.88	24.48	-3.27	21.21	15.3
4 <sup>f</sup>	-43.34	-51.23	0.29	-50.94	-46.6
4 <sup>g</sup>	52.62	31.08	-3.65	27.43	27.7
5 <sup>f</sup>	-64.53	-69.80	5.06	-64.74	
5 <sup>g</sup>	35.05	12.86	0.57	13.43	
6 <sup>f</sup>	0.18	2.6	-5.12	-2.52	
6 <sup>g</sup>	40.34	45.84	-1.42	44.42	
7 <sup>f</sup>	-10.39	0.03	-4.73	-4.70	
7 <sup>g</sup>	46.67	49.47	-2.75	46.72	

<sup>a</sup> Ab initio SCF/DZP value. <sup>b</sup> Ab initio MP2/DZP//SCF/DZP value.

<sup>c</sup> Zero-point energy contribution obtained at the SCF/DZP level and scaled by 0.9. <sup>d</sup> Ab initio MP2/DZP//SCF/DZP plus zero point energy correction value. <sup>e</sup> Ab initio MP4/6-311++G\*\*//MP2/6-311G\*\* +  $\Delta \text{ZPE}$  from ref 10. <sup>f</sup> Reaction energy. <sup>g</sup> Activation energy.

species<sup>5</sup> can be written as

$$\frac{d[\text{CHCl}_3]}{dt} = -k_1[\text{CHCl}_3][\text{OH}^-] \quad k_1 = 1.1 \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}$$

For reaction 5, we can use transition-state theory to estimate the reaction rate. We found that (for  $T = 318 \text{ K}$ )

$$\Delta G^\circ = 21.83 \text{ kcal/mol}$$

$$k_2 = 4(kT/h)e^{-\Delta G^\circ/kT}$$

$$k_2 = 2.6 \times 10^{-2} \text{ L mol}^{-1} \text{ s}^{-1}$$

The factor 4 in  $k_2$  is due to four equivalent transition-state structures with equal energy. Considering initially that (as reported in ref 5)

$$[\text{OH}^-]_0 = 0.0489 \text{ mol/L}$$

$$[\text{CHCl}_3]_0 = 0.01195 \text{ mol/L}$$

and supposing that  $[\text{OH}^-]$  remain constant and also that  $[\text{H}_2\text{O}] = 55.6 \text{ mol/L}$ , we can write, based on the Robinson's experiment<sup>5</sup> and on Scheme 1, the following kinetics equations:

$$\frac{d[\text{CHCl}_3]}{dt} = -k'_1[\text{CHCl}_3]$$

$$\frac{d[\text{CCl}_2]}{dt} = k'_1[\text{CHCl}_3] - k'_2[\text{CCl}_2]$$

$$\frac{d[\text{CO}]}{dt} = k'_2[\text{CCl}_2]$$

with

$$k'_1 = 5.4 \times 10^{-5} \text{ s}^{-1}$$

$$k'_2 = 1.4 \text{ s}^{-1}$$

As  $k'_2 \gg k'_1$ , we will have only a small concentration of  $\text{CCl}_2$  in solution, and according to the stationary-state approximation, we can write

$$d[\text{CCl}_2]/dt = 0$$

$$d[\text{CO}]/dt = k'_1[\text{CHCl}_3]$$

So, the rate of formation of CO is equal to the rate of disappearance of  $\text{CHCl}_3$ , a result obtained by Robinson (see Figure 2 in ref 5). Some uncertainties may exist in our  $\Delta G^\circ$  calculated value. Supposing an uncertainty of  $\Delta(\Delta G^\circ) = \pm 5 \text{ kcal/mol}$ , we will have

$$k'_2 = 5.1 \times 10^{-4} - 3.8 \times 10^3 \text{ s}^{-1}$$

As can be seen, yet the same general picture of the reaction remains ( $k'_2 \gg k'_1$ ). We can conclude that our results lead to a reaction mechanism in agreement with experimental observations.

## Conclusions

We have performed ab initio calculations in order to determine the mechanism of  $\text{CCl}_2$  decomposition in basic aqueous solutions. We have shown that the first step is slow and corresponds to insertion of  $\text{CCl}_2$  into the O-H bond, forming  $\text{CHCl}_2\text{OH}$ . Then, this loses HCl, in an  $\text{OH}^-$ -catalyzed mechanism, forming  $\text{ClCHO}$ . Again, the  $\text{OH}^-$  catalytic effect eliminates HCl, resulting in the final product, carbon monoxide.

The transition state theory was used to calculate the rate constant of the  $\text{H}_2\text{O} + \text{CCl}_2$  reaction. The calculated rate constant was shown to be in agreement with the kinetics of basic aqueous decomposition of  $\text{CHCl}_3$ .

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