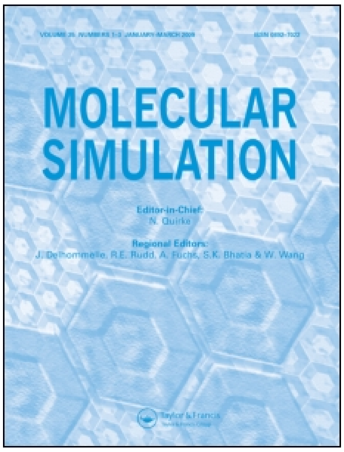

Molecular Simulation
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

A Density Functional Theory Study of the Reactions of Dichlorocarbene and Isodichloromethane with H_2O

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To cite this Article Li, Yun-Liang , Zuo, Peng and Phillips, David Lee(2004) 'A Density Functional Theory Study of the Reactions of Dichlorocarbene and Isodichloromethane with H_2O', Molecular Simulation, 30: 2, 173 — 178

To link to this Article: DOI: 10.1080/0892702031000152109

URL: http://dx.doi.org/10.1080/0892702031000152109

Molecular Simulation, Vol. 30 (2–3), 15 February–15 March 2004, pp. 173–178

A Density Functional Theory Study of the Reactions of Dichlorocarbene and Isodichloromethane with H_2O

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(Received October 2002; In final form December 2002)

A density functional theory investigation of the reactions of dichlorocarbene and isodichlorocarbene with H_2O is reported. The reactions are found to be noticeably different for dichlorocarbene and isodichloromethane and can be attributed to their different structures and properties. The isodichloromethane species can react with H_2O by both direct and indirect O–H insertion reactions with the indirect reaction having a much lower barrier to reaction than the direct reaction. However, the dichlorocarbene reacts with H_2O predominantly via a direct OH insertion reaction that has a barrier to reaction noticeably lower than both of the isodichloromethane reactions.

Keywords: Density functional theory; Dichlorocarbene; Isodichloromethane; Water; OH insertion reaction

INTRODUCTION

The chemistry and photochemistry of polyhalomethane molecules are of interest in atmospheric chemistry as sources of reactive halogen molecules [1–3] and in synthetic chemistry for use as reagents for the cyclopropanation of olefins and diiodomethylation of carbonyl compounds [4–7]. Ultraviolet excitation of a number of polyhalomethane molecules in condensed phase environments produces photoproduct(s) that have characteristic and intense transient absorption bands in the ultraviolet and visible wavelengths that were tentatively assigned to several probable species like radicals, radical cations and isomers [8–10]. Recent femtosecond absorption experiments indicate the photoproduct species is formed by solvent induced geminate recombination of the initially produced fragments [11–13]. Time-resolved resonance Raman spectroscopy (TR^3) experiments demonstrated that isopolyhalomethane products were mainly responsible for the intense transient absorption bands observed on the ultrafast to nanosecond time-scales in liquid solutions [14–18].

The chemical reactivity of isopolyhalomethane photoproduct species were investigated using both theory and experiment and it was found that these species can be effective carbenoid species in several cases [19–23]. For example, DFT calculations showed isodiiodomethane ($CH_2I{-}I$) was found to easily react with ethylene to give a cyclopropane product and leaving group via a single step reaction with a low barrier of about 2.9 kcal/mol [19]. TR^3 experiments done under conditions similar to the original photochemical studies that produced norcarane (the cyclopropanated product of cyclohexene) demonstrated $CH_2I{-}I$ reacts with cyclohexene on the 5–10 ns time scale and then immediately forms a I_2:cyclohexene complex (from the I_2 leaving group and the cyclohexene solvent [21]). This and the DFT results indicate that the $CH_2I{-}I$ species is the major methylene transfer agent for cyclopropanation reactions employing the ultraviolet photolysis of diiodomethane in the presence of olefins, and a reaction mechanism was proposed [5,19,21].

Carbenes and carbenoid species can also undergo OH insertion reactions with alcohols and water [24,25]. Recent *ab initio* calculations for the dichlorocarbene (CCl_2) species with one water molecule showed that CCl_2 undergoes direct OH insertion via a barrier of about 13.4 kcal/mol [26]. In this paper, we report the first theoretical investigation of the reaction of an isopolyhalomethane species with water in order to explore its possible OH insertion

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ISSN 0892-7022 print/ISSN 1029-0435 online © 2004 Taylor & Francis Ltd
DOI: 10.1080/0892702031000152109

reactions analogous to that of carbenes. We present results for the reactions of the CH_2Cl-Cl species with one water molecule and compare this to the related reaction previously reported for the CCl_2 carbene species [26]. The different structures and properties of the CH_2Cl-Cl and CCl_2 species lead to substantial differences in their reactions with the water molecule. We briefly discuss the similarities and differences in the chemical reactivity of CCl_2 and CH_2Cl-Cl with H_2O.

COMPUTATIONAL DETAILS

All of the density functional theory (DFT) and *ab initio* calculations reported here employed the Gaussian 98 program suite [27]. The DFT calculations used the B3LYP method [28,29] and the 6-311G** basis set. The geometry of the reactants, intermediates, transition states and products were fully optimized with cutoffs of 0.000450 and 0.000300 hartree/bohr for the maximum force and its root mean square, respectively. MP2/DZP//SCF/DZP calculations were also done for the dichlorocarbene reaction with water to produce $CHCl_2OH$ and water products for comparison to previous *ab initio* work for this reaction and to check the reliability of the DFT calculations for these OH insertion reactions. Analytical frequency computations were done to confirm the optimized structures to be either a minimum or first-order saddle point. Intrinsic reaction coordinate (IRC) calculations [30] were performed to confirm the transition states connected the related reactants and products.

RESULTS AND DISCUSSION

Reaction of $CCl_2 + H_2O$

The optimized geometry for all the stationary states were fully optimized using B3LYP/6-311G** and MP2/DZP//SCF/DZP levels of theory for the reaction of $CCl_2 + H_2O$ to give $CHCl_2OH$ product. Figure 1 presents schematic diagrams of the optimized geometry for the species involved in the reaction with the values of selected key parameters given. Figure 1 also presents the relative energies of these species (in kcal/mol). The two different computational methods gave similar optimized geometry and barriers to reaction (about 14.7 kcal/mol for B3LYP/6-311G** and about 13.4 kcal/mol for MP2/DZP//SCF/DZP which is very close to 13.43 kcal/mol reported previously from *ab initio* calculations from another group [26]). One noticeable difference between the DFT and *ab initio* methods is that the DFT method predicts an initial formation of a weak complex species (IM1). MP2/DZP//SCF/DZP calculations did not easily converge when the min1 B3LYP/6-311G** geometry was used. Our results using the two different methods suggest that the complex formation is very weak and does not significantly change the barrier to reaction or the reaction pathway very much. Inspection of TS1 suggests that donation of the carbon lone pair to hydrogen and a donation of the oxygen lone pair to the carbene unoccupied π orbital consistent with the direct OH insertion mechanism previously postulated [26]. TS2 essentially occurs to take the reaction system to a more stable conformation of the $CHCl_2OH$ molecule.

Reaction of CH_2Cl-Cl with H_2O and Comparison to the $CCl_2 + H_2O$ Reaction

Our B3LYP/6-311G** computational results for the reactions of CCl_2 with H_2O display reasonable agreement with previous *ab initio* results for this reaction and this provides us with some confidence that similar calculations will be useful to explore the chemical reactivity of isopolyhalomethanes, like CH_2Cl-Cl, with water. The optimized geometry of the stationary structures and the relative energies of the reaction of CH_2Cl-Cl with H_2O are shown in Fig. 2. Comparison of Figs. 1 and 2 reveals that the reactions of CH_2Cl-Cl with H_2O are noticeably different from that of CCl_2 and this can be attributed to their differences in structure and properties. Both Cl atoms are bonded to the C atom in CCl_2 and its reaction with H_2O does not have a leaving group and results in a direct O−H insertion reaction to give a $CHCl_2OH$ molecule. However, CH_2Cl-Cl has only one Cl atom attached to the C atom. CH_2Cl-Cl also contains two C−H bonds and a weak Cl−Cl bond. This leads to two different reactions that have either a Cl_2 or a HCl leaving group when producing a CH_3OH and CH_2ClOH products respectively. It is very difficult for the C−Cl bond to be broken and the CH_2Cl-Cl reaction with H_2O to produce CH_3OH and Cl_2 occurs with a high barrier of about 40.4 kcal/mol. This reaction occurs directly via a single step and transfers a CH_2 group to the O−H bond and has a Cl_2 leaving group. Thus, this reaction is analogous to the cyclopropanation reaction with olefins previously observed for several isopolyhalomethanes [18–20,23]. However, these cyclopropanation reactions with olefins generally occurred with low barriers to reactions [18–20,23]. A two step reaction mechanism was found to occur much more easily (about 16.5 kcal/mol accumulative barrier) in Fig. 2 and produces a CH_2ClOH product with a HCl leaving group. In this reaction the C−Cl−Cl angle changes to become about 180° in TS4 and can then continue on to eventually attack the H atom of the H_2O molecule (which has its O atom bonded to

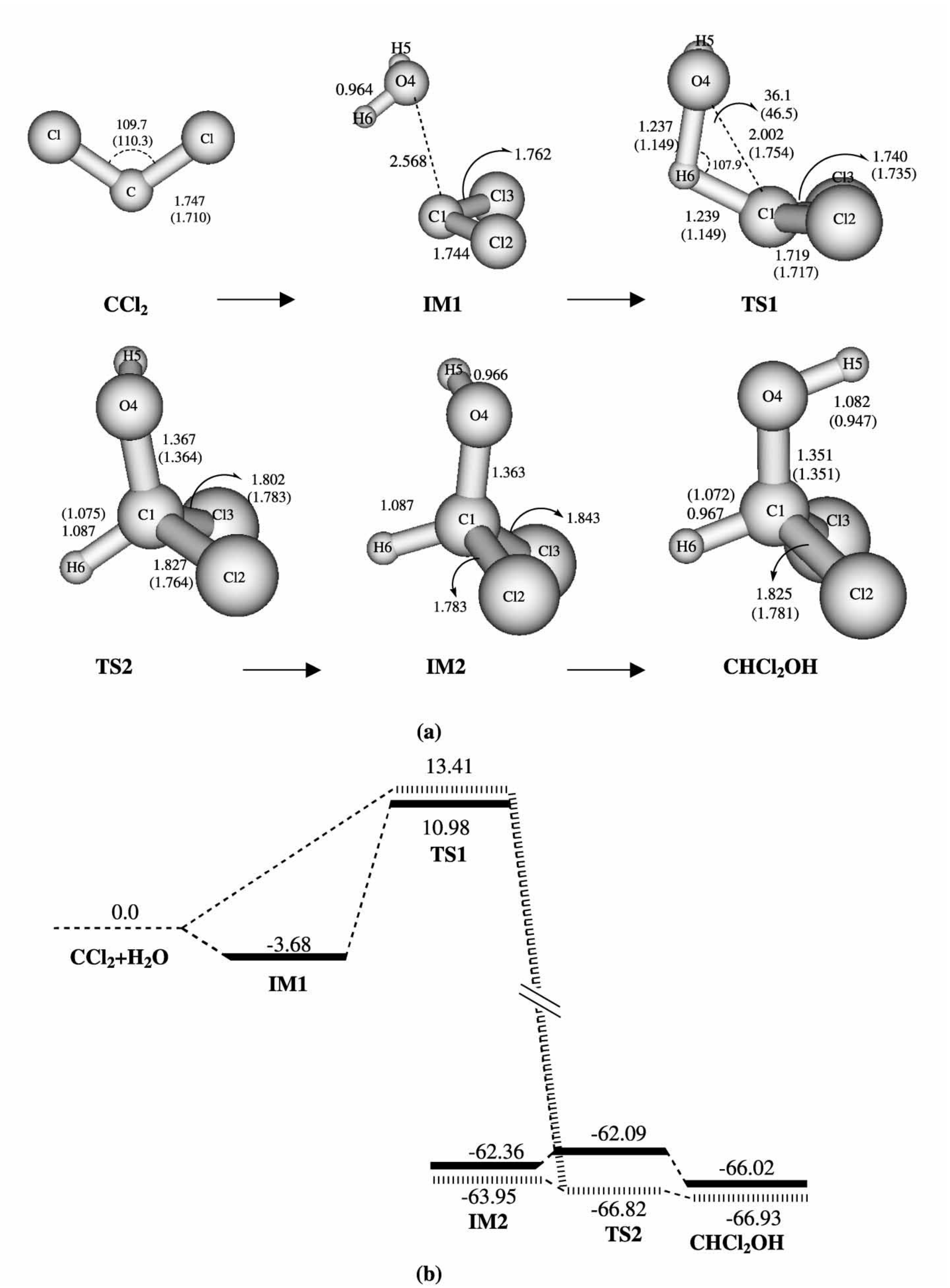

FIGURE 1 (a) Schematic diagram displaying the B3LYP/6-311G** optimized geometry for selected reactants, intermediates, transition states and products for the reaction of $CCl_2 + H_2O$ to produce $CHCl_2OH$. Selected geometry parameters are also given with bond lengths in Å and bond angles in degrees. The numbers in parentheses are values from MP2/6-311++G** calculations. (b) Relative energy profiles are shown for the $CCl_2 + H_2O \rightarrow CHCl_2OH$ reaction from B3LYP/6-311G** (solid lines) and MP2/DZP//SCF/DZP (dashed lines) levels of theory.

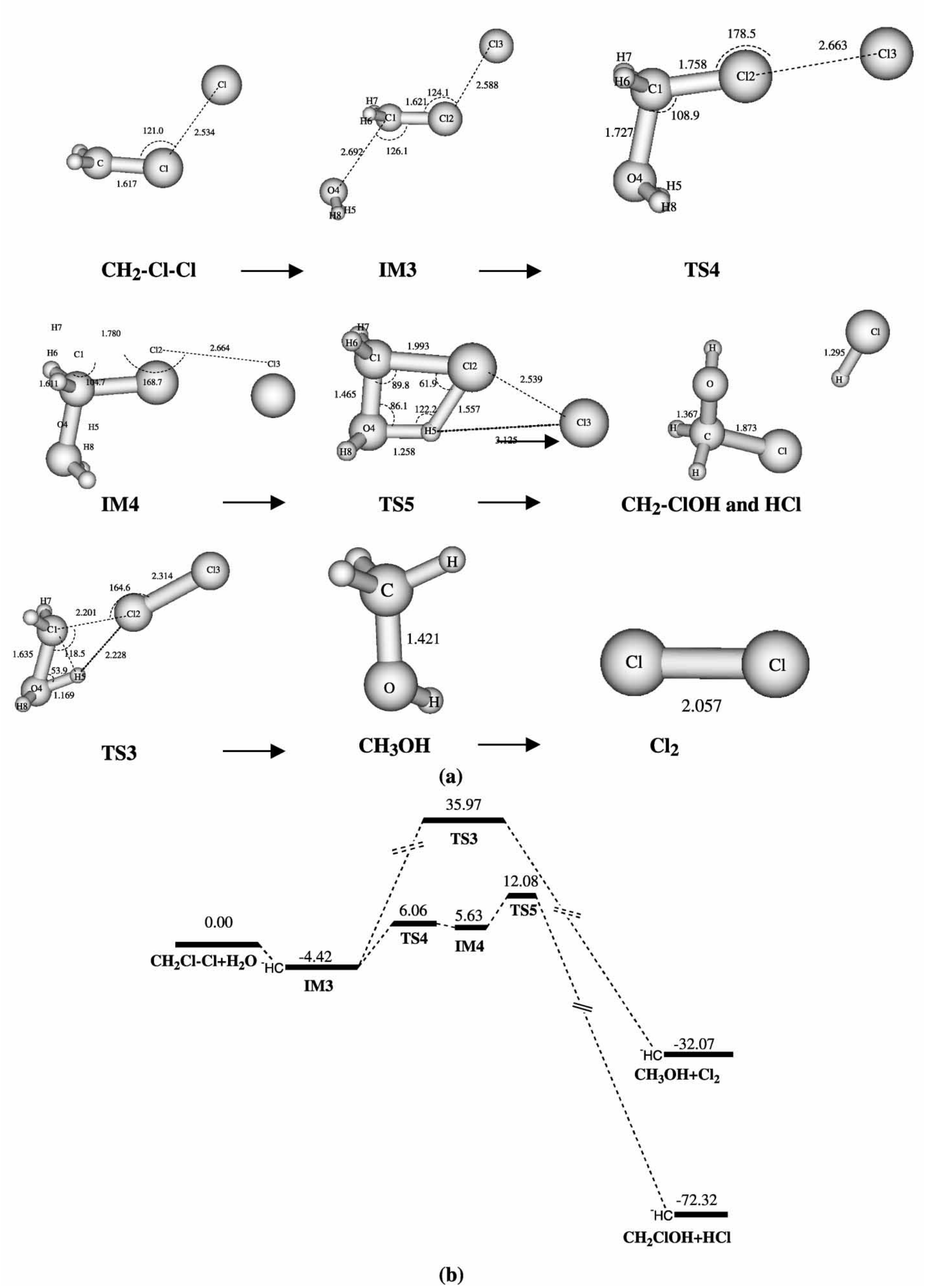

FIGURE 2 (a) Schematic diagram displaying the B3LYP/6-311G** optimized geometry for selected reactants, intermediates, transition states and products for the reactions of $CH_2Cl–Cl + H_2O$. Selected geometry parameters are also given with bond lengths in Å and bond angles in degrees. (b) Relative energy profiles are shown for the $CCl_2 + H_2O$ reactions from B3LYP/6-311G** calculations.

the C atom of CH_2Cl-Cl) and form a HCl molecule leaving group and CH_2ClOH product.

Inspection of the structure of TS3 relative to IM3 in Fig. 2 reveals that the C^1-Cl^2 bond length increases from 1.621 Å in IM3 to 2.201 Å in TS3 and the C^1-O^4 bond length decreases from 2.692 Å in IM3 to 1.635 Å in TS3. This indicates there is partial cleavage of the C^1-Cl^2 bond and partial formation of the C^1-O^4 bond in TS3. This is accompanied by partial formation of the C^1-H^5 bond. The Cl^2-Cl^3 bond decreases from 2.588 Å in IM3 to 2.314 Å in TS3 and suggests the Cl–Cl bond becomes stronger in TS3. These changes upon going from IM3 to TS3 are consistent with a direct O–H insertion reaction mechanism similar to that of the $CCl_2 + H_2O$ reaction which also has partial O–H bond cleavage and C–O and C–H bond formation in its transition state (TS1). However, the $CCl_2 + H_2O$ reaction has a much lower barrier to reaction to produce the $CHCl_2OH$ product (about 14.66 kcal/mol) compared to the $CH_2Cl-Cl + H_2O$ reaction to make $CH_3OH + Cl_2$ (about 40.4 kcal/mol). The larger barrier for the latter reaction is mainly due to the need to break a very strong C–Cl bond in CH_2Cl-Cl during the O–H insertion reaction while the former reaction does not need to break a C–Cl bond. It is interesting to note that CH_2Cl-Cl reacts with ethylene to give a cyclopropane product and Cl_2 leaving group with a moderate barrier of about 8.9 kcal/mol from B3LYP/ccpVTZ calculations [20]. The barrier in this cyclopropanation reaction is substantially smaller than the $CH_2Cl-Cl + H_2O$ direct O–H insertion reaction mostly due to the C–Cl bond cleavage being offset by formation of two C–C bonds in the cyclopropanation reaction.

The second reaction pathway found for $CH_2Cl-Cl + H_2O$ is an indirect O–H insertion reaction that involves two steps via formation of an intermediate, IM4, that then goes on to $CH_2ClOH + HCl$ products. The C^1-O^4 bond length and C–Cl–Cl and $Cl^2-C^1-O^4$ bond angles change from 2.692 Å, 124.1°, 126.1°, respectively, in IM3 to 1.727 Å, 178.5°, and 108.9°, respectively, in TS4. This indicates there is partial C–O bond formation and the terminal Cl atom undergoes substantial rotation. This is accompanied by some weakening of the C^1-Cl bond from 1.621 to 1.758 Å. As TS4 goes on to the nearby intermediate IM4 the structure changes moderately to continue the rotation of the terminal Cl atom toward the O–H bond and the C^1-Cl bond weakens to 1.780 Å while the C–O bond strengthens to 1.611 Å in IM4. IRC calculations confirmed TS4 connected IM3 to IM4 and vibrational analysis found one imaginary frequency $190.3i\,cm^{-1}$ with a reaction vector of $0.19\ R_{C}1-_{Cl}2\ -0.48\ R_{C}l-_{O}4-0.32\ R_{C}1-_{H}5\ -0.32\ R_{C}1-_{H}8+0.59\ A_{C}1-_{Cl}2-_{Cl}3$ that is consistent with the structural changes occurring as IM3 goes to TS4 and IM4. In order to go from IM4 to the products, the reaction goes through a cyclic transition state, TS5, which helps to simultaneously weaken the C–Cl bond and transfer the H atom from O to C. Inspection of TS5 shows that the C–O bond strengthens to 1.465 Å, the O^4-H^5 bond weakens to 1.258 Å, the C–Cl bond weakens further to 1.993 Å, and H–Cl bonds becomes partially formed with 1.557 and 3.125 Å bond lengths. This cyclic TS5 helps couple the C–Cl bond and O–H bond cleavage processes to the simultaneous C–O and H–Cl bond formation. It is interesting to note that the middle Cl atom acts as a transfer agent for the hydrogen atom that eventually ends up on the terminal Cl atom when TS5 goes on to the $CH_2ClOH + HCl$ final product. This cyclic TS5 and its properties help lower the barrier to reaction substantially for an accumulated barrier of about 16.5 kcal/mol from IM3 to TS5 to give $CH_2ClOH + HCl$ products. The direct O–H insertion pathway ($CH_2Cl-Cl + H_2O \rightarrow CH_3OH + Cl_2$ products) has a much higher barrier of about 40.4 kcal/mol.

We note that both the direct and indirect O–H insertion reactions of CH_2Cl-Cl with H_2O take place with higher barriers to reaction (about 40.4 and 16.5 kcal/mol, respectively) than the $CCl_2 + H_2O$ direct O–H insertion reaction (about 14.66 kcal/mol). This suggests that isopolyhalomethanes are not as effective as dihalocarbenes for O–H insertion reactions although the indirect reaction pathway barrier is only moderately higher. Recent *ab initio* calculations suggested that an additional H_2O molecule can substantially alter and catalyze the O–H insertion reaction of CCl_2 with water [31]. This study found that reaction of $CCl_2 + 2H_2O$ took place via a small barrier to reaction of about 3.34 kcal/mol from MP2/DZP calculations [31]. It is not clear how additional water molecules may catalyze the O–H insertion reactions of CH_2Cl-Cl with water and this will be investigated in the future.

Acknowledgements

This research has been supported by grants from the Research Grants Council of Hong Kong (HKU 7087/01P) and the Committee for Research and Conference Grants (CRCG) of the University of Hong Kong.

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