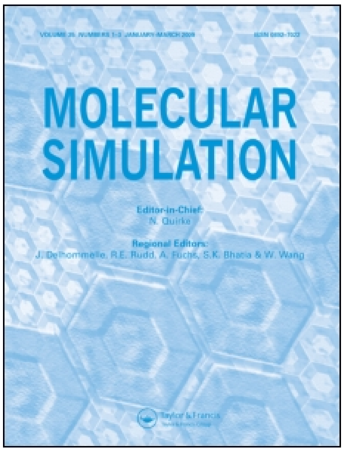

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An *ab initio* study of the reactions of CH_2X-X (X=Cl, Br, I) isopolyhalomethanes with nCH_3OH

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An *ab initio* study of the reactions of $CH_2X{-}X$ (X=Cl, Br, I) isopolyhalomethanes with nCH_3OH

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An *ab initio* investigation of the reactions of the $CH_2X{-}X$ (X=Cl, Br, I) isodihalomethanes with nCH_3OH is reported. The reactions are found to be catalyzed by the methanol molecules and the barriers to reaction increase as the halogen atoms are varied from Cl to Br to I.

Keywords: *Ab initio*; Isodihalomethane; Methanol; OH insertion reaction

1. Introduction

Polyhalomethane molecules are of interest in a wide range of areas including atmospheric chemistry (as sources of reactive halogen molecules) [1–3] and synthetic chemistry (as reagents for the cyclopropanation of olefins and diiodomethylation of carbonyl compounds) [4–7]. Ultraviolet photolysis of a number of polyhalomethanes in the condensed phase results in photoproduct(s) that have characteristic and intense transient absorption bands in the ultraviolet and visible wavelengths [8–10]. Recent femtosecond time-resolved absorption experiments indicate these photoproduct species are produced by solvent induced geminate recombination of the initially formed fragments [11–13]. Time-resolved resonance Raman spectroscopy (TR^3) experiments showed that the intense transient absorption bands observed on the ultrafast to nanosecond time-scales in liquid solutions were mostly due to isopolyhalomethane products [14–18].

Both theory and experiment were utilized to examine the chemical reactivity of the isopolyhalomethane photoproduct species. It was discovered that these species can be effective carbenoids for cyclopropanation of olefins [19–23]. For instance, density functional theory (DFT) calculations found that isodiiodomethane ($CH_2I{-}I$) can readily react with ethylene to produce a cyclopropane product and I_2 leaving group via a single step reaction with a low barrier of about 2.9 kcal/mol [19]. The TR^3 experiments were also done under conditions similar to the original photochemical studies that produced norcarane (the cyclopropanated product of cyclohexene) [21]. These TR^3 experiments showed that $CH_2I{-}I$ reacts with cyclohexene on 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 calculation results indicates that the $CH_2I{-}I$ species is the predominant methylene transfer agent for cyclopropanation reactions utilizing the ultraviolet photolysis of CH_2I_2 in the presence of olefins [5, 19, 21]. A reaction mechanism was proposed to account for the experimental and computational results [5, 19, 21].

It is known that carbenoid species as well as carbenes can also undergo OH insertion reactions with alcohols and water [24, 25]. Recent picosecond TR^3 experiments have directly observed the reaction of isobromoform with water to form a $CHBr_2OH$ product via an O—H insertion reaction [26, 27]. A combined experimental and theoretical study also found that $CH_2I{-}I$ can react with water via an O—H insertion/HI elimination reaction [28] More recently, *ab initio* calculations also indicate that $CH_2I{-}I$ can react with methanol (CH_3OH) by an O—H insertion/HI elimination reaction to produce a iodoether (CH_3OCH_2I) product and an HI leaving group [29]. In this paper, we use *ab initio* calculations to study the $CH_2X{-}X$ (X=Cl, Br, I) $+ nCH_3OH$ ($n = 1, 2, 3$) reactions and examine how the identity and properties of the halogen atom influences these types of O—H insertion/HX elimination reactions.

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2. Computational details

All of the *ab initio* calculations reported here utilized the Gaussian 98 program suite [30]. The MP2 method was used in the calculations. The 6-31G* basis set was employed for all the C, H, O, Cl and Br atoms and the lanl2dz basis set with a *d* polarization of 0.266 was used for the I atoms. The geometry of the reactants, intermediates, transition states and products were fully optimized. Analytical frequency computations were done to confirm the optimized structures to be either a minimum or first-order saddle point and to obtain the zero-point energies. Intrinsic reaction coordinate (IRC) calculations [31] were done to confirm the transition states connected the related reactants and products.

3. Results and discussion

3.1 Reaction of $CH_2X—X$ (X=Cl, Br, I) + nCH_3OH

The optimized geometries for all the stationary states were fully optimized. Figures 1–3 presents schematic diagrams for the optimized geometry for the stationary structures found for the $CH_2X—X$ (X=Cl, Br, I) + nCH_3OH reactions. Figure 4 presents schematic diagrams for the relative energy profiles for the $CH_2X—X$ (X=Cl, Br, I) + nCH_3OH reactions from the MP2 calculations. Examination of figures 1–3 reveals that the reactant complexes (RCs) have some moderate H—X (where X=Cl, Br, I) and C—O interactions between the isopolyhalomethane species and the methanol molecule(s) accompanied by some lengthening of the X—X bond compared to their starting materials. These changes are consistent with the methanol molecule(s) stabilizing the reaction system and the relative energies of the RCs being lower than the starting materials (SMs) in figure 4.

As the RCs proceed towards their respective transition states (TSs) the H—X and C—O distances decrease noticeably indicating there is partial H—X and C—O bond formation in the TSs. For example, the H—Br and C—O distances go from 2.509–2.843 Å in RC21 to 2.245 and 2.236 Å in TS21 for the $CH_2Br—Br + CH_3OH$ reaction. These changes in the H—X and C—O distances are accompanied by a significant weakening of the X—X bond suggesting this bond is starting to break. For example, the Br—Br distance goes from 2.689 Å in RC21 to 2.878 Å in TS21 for the $CH_2Br—Br + CH_3OH$ reaction. The changes in the H—X, C—O and X—X distances as the RCs go to their respective TSs are consistent with an O—H insertion/HX elimination reaction occurring and this is similar to O—H insertion/HI elimination reactions previously observed for isodiiodomethane ($CH_2I—I$) with both H_2O and methanol solvent molecules [28, 29].

Inspection of figures 2 and 3 reveals that as the number of methanol molecules explicitly involved in the reaction system, the RCs and TSs have cyclic structures with increasing hydrogen-bonding interactions. In the RCs, the H—X interaction becomes stronger as the number of methanol molecules increases in the reaction system. For example, the HBr distance decreases from 2.509 Å in RC21 with one methanol molecule to 2.395 Å in RC23 with three methanol molecules for the $CH_2Br—Br$ + nCH_3OH reactions. This is consistent with greater solvent stabilization of the RCs as more methanol molecules are added. This leads to the relative energies going from −7.7 kcal/mol for RC21 with one methanol molecule to −30.2 kcal/mol for RC23 with three methanol molecules as shown in figure 4 for the $CH_2Br—Br + nCH_3OH$ reactions as an example.

Inspection of the relative energies for the $CH_2X—X$ + nCH_3OH reactions in figure 4 reveals that as the number of methanol molecules in the reaction system increases, the reaction barrier decreases. For example, the barrier to reaction from RC31 to TS31 is 9.9 kcal/mol for the $CH_2I—I + CH_3OH$ reaction and decreases to 6.1 kcal/mol from RC33 to TS33 for the $CH_2I—I + 3CH_3OH$ reaction. A similar trend is found in the Br case where the barrier to reaction from RC21 to TS21 is 4.1 kcal/mol for the $CH_2Br—Br + CH_3OH$ reaction and decreases to 2.8 kcal/mol from RC23 to TS23 for the $CH_2Br—Br$ + 3 CH_3OH reaction. These changes observed in the barriers to reaction suggest that addition of the methanol molecules is catalyzing the O—H insertion/HX elimination reaction. This is similar to what we have previously observed for the O—H insertion/HI elimination reactions for isodiiodomethane ($CH_2I—I$) with both H_2O and methanol solvent molecules [28, 29].

As the methanol molecules are added to the reaction system, there tends to be smaller structural changes

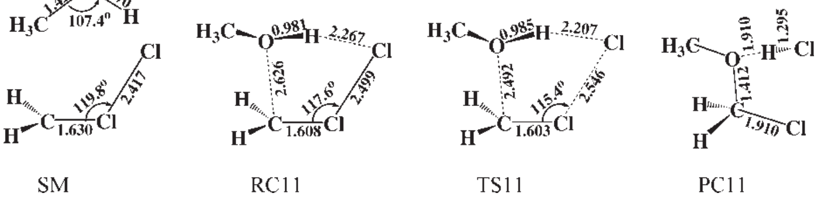


Figure 1. Schematic diagram displaying the MP2 optimized geometry for selected reactants, intermediates, transition states and products for the reaction of $CH_2Cl—Cl + CH_3OH \rightarrow CH_2Cl—O—CH_3 + HCl$. Selected geometry parameters are also given with bond lengths in Å and bond angles in degrees.

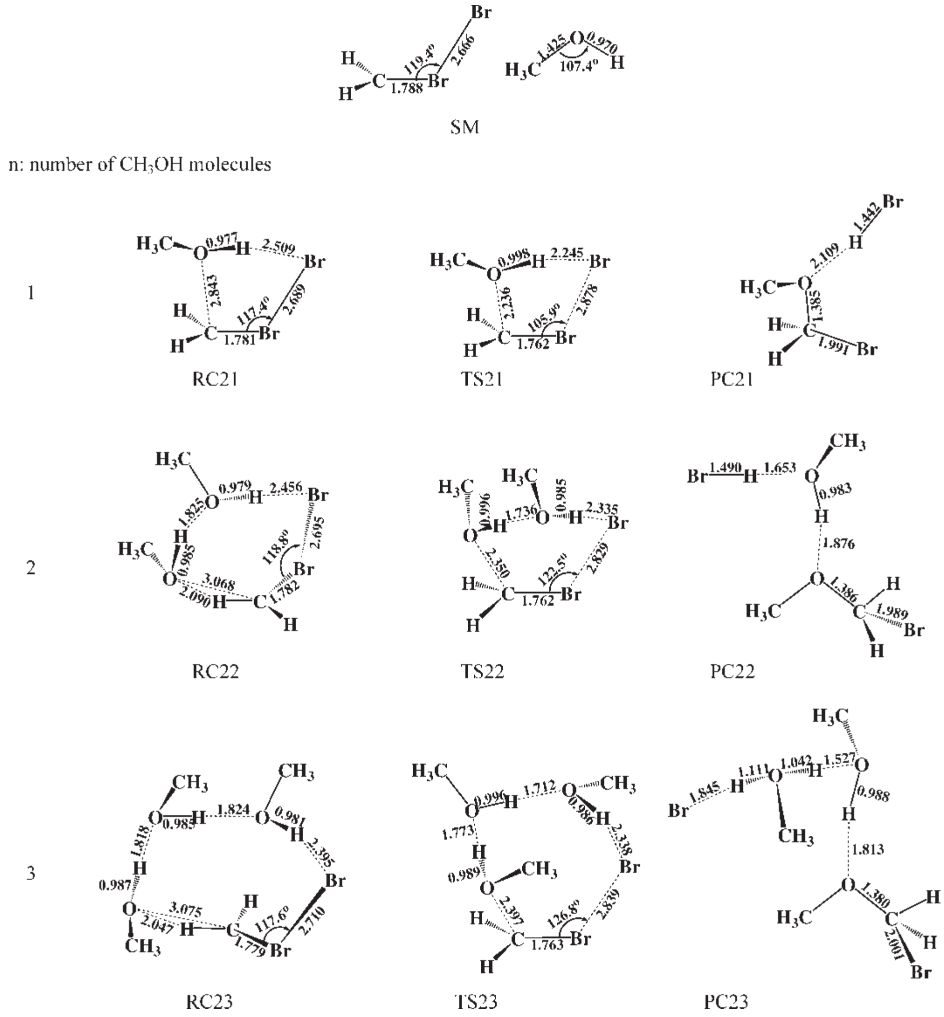


Figure 2. Schematic diagram displaying the MP2 optimized geometry for selected reactants, intermediates, transition states and products for the reaction of CH$_2$Br—Br + nCH$_3$OH → CH$_2$Br—O—CH$_3$ + HBr + $(n-1)$CH$_3$OH where $n = 1, 2, 3$. Selected geometry parameters are also given with bond lengths in Å and bond angles in degrees.

occurring as the reaction proceeds from its RC to its TS. For example, the changes in the H—Br distance as the reactions go from the RCs to their respective TSs are −0.264 Å from RC21 to TS21 (for one methanol molecule), −0.121 Å from RC22 to TS22 (for two methanol molecules) and −0.057 Å from RC23 to TS23 (for three methanol molecules) for the CH$_2$Br—Br + nCH$_3$OH reactions as an example. Similarly, the changes in the Br—Br distance as the reactions go from the RCs to their respective TSs are +0.189 Å from RC21 to TS21 (for one methanol molecule), +0.134 Å from RC22 to TS22 (for two methanol molecules) and +0.0129 Å from RC23 to TS23 (for three methanol molecules) for the CH$_2$Br—Br + nCH$_3$OH reactions. Similar trends are also observed for the CH$_2$I—I + nCH$_3$OH reactions. The smaller structural changes observed in going from the RCs to their respective TSs as the number of methanol molecules increases suggest less energy will be needed to go from the RCs to their TSs and this is consistent with methanol catalyzing these reactions.

3.2 Comparison of the Reactions of CH$_2$X—X (X=Cl, Br, I) + nCH$_3$OH and Influence of the Halogen Atoms

Inspection of figures 1–3 reveals there are some noticeable trends as the halogen atoms are varied from Cl to Br to I. In the RCs, the H—X distance becomes weaker as one goes from Cl to Br to I. For example, the H—Cl distance in RC11 is 2.267 Å, the H—Br distance in RC21 is 2.509 Å and the H—I distance 2.882 Å in RC31. These changes are accompanied by weaker C—O interactions as the halogens are varied from Cl to Br to I. For example, the C—O distances are 2.626 Å in RC11 (X=Cl), 2.843 Å in RC21 (X=Br) and 3.167 Å in RC31 (X=I) for the CH$_2$X—X + CH$_3$OH reactions. The weaker H—X and C—O interactions as the halogens vary from Cl to Br to I correlate with the stabilization energies observed for the RCs which have values of −7.8 kcal/mol for RC11 (X=Cl), −7.7 kcal/mol for RC21 (X=Br) and −6.4 kcal/mol for RC31 (X=Cl).

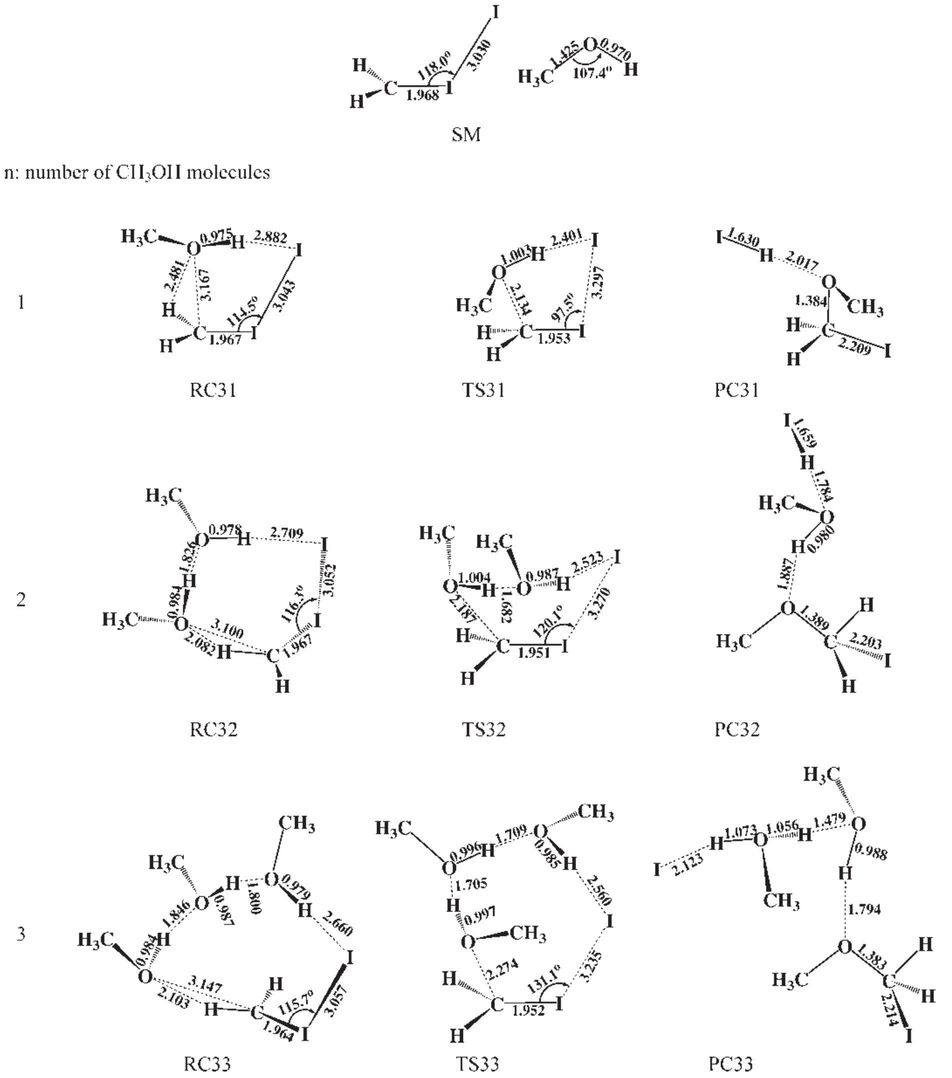
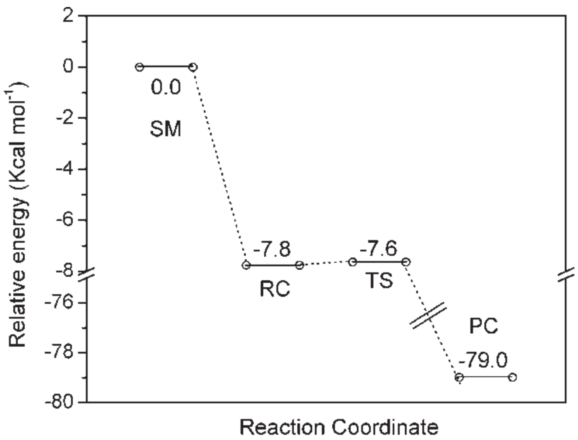


Figure 3. Schematic diagram displaying the MP2 optimized geometry for selected reactants, intermediates, transition states and products for the reaction of $CH_2I—I + nCH_3OH \rightarrow CH_2I—O—CH_3 + HI + (n-1)CH_3OH$ where $n = 1, 2, 3$. Selected geometry parameters are also given with bond lengths in Å and bond angles in degrees.

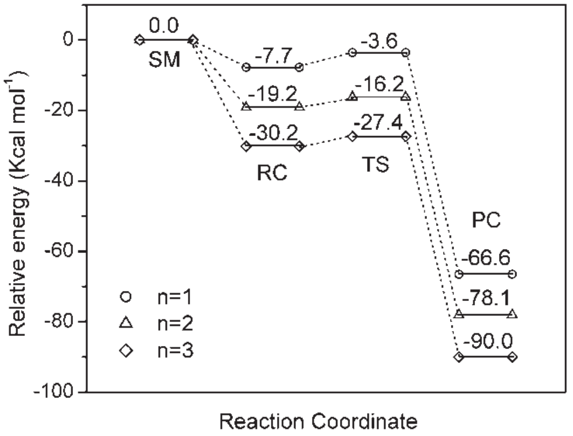
This suggests that greater H—X and C—O interactions are largely responsible for the stabilization of the RCs and the RCs will be stabilized more by the more electronegative halogen atoms (Cl > Br > I).

The TSs also show noticeable trends in their structures as the halogen atoms are varied from Cl to Br to I. The H—X distances become weaker and go from 2.207 Å in TS11 (X=Cl) to 2.245 Å in TS21 (X=Br) to 2.401 Å in TS31 (X=I). The C—O bond formation becomes stronger and go from 2.492 Å in TS11 (X=Cl) to 2.236 Å in TS21 (X=Br) to 2.134 Å in TS31 (X=I). These changes indicate that the H—X interaction becomes weaker while the C—O interaction becomes stronger in the TSs as the halogen atoms are varied from Cl to Br to I.

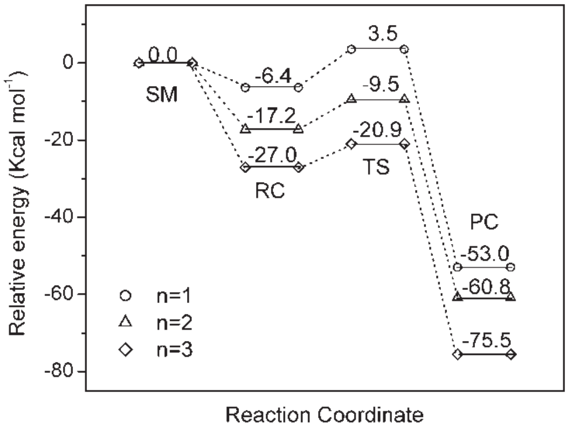
As the RCs go to their respective TSs, the changes in the structures also exhibit trends as the halogen atoms are varied from Cl to Br to I. The change in the H—X distances as the RCs go to their respective TSs are − 0.060 Å from RC11 to TS11 (X=Cl), − 0.264 Å from RC21 to TS21 (X=Br) and − 0.481 Å from RC31 to TS31 (X=I). The change in the C—O distances as the RCs go to their respective TSs are − 0.134 Å from RC11 to TS11 (X=Cl), − 0.607 Å from RC21 to TS21 (X=Br) and − 1.033 Å from RC31 to TS31 (X=I). The changes in the X—X distances as the RCs go to their respective TSs are + 0.047 Å from RC11 to TS11 (X=Cl), + 0.189 Å from RC21 to TS21 (X=Br) and + 0.254 Å from RC31 to TS31 (X=I). The smallest structural changes as the RCs go to their respective TSs occur for X=Cl. These barriers to reaction become larger for X=Br and even larger for I (e.g. Cl < Br < I) and suggests that less energy is required to go from the RC to the TS for the X=Cl compared to X=Br and in turn compared to X=I. These structural changes correlate well with the trends in the barriers to reaction from the RCs to their respective TSs. The barriers to reaction are 0.2 kcal/mol from RC11 to TS11 for the $CH_2Cl—Cl + CH_3OH$ reaction, 4.1 kcal/mol from RC21 to TS21 for the $CH_2Br—Br + CH_3OH$ reaction, and 9.9 kcal/mol from RC31 to TS31 for the $CH_2I—I + CH_3OH$ reaction. Smaller structural changes from the RCs to TSs correlate with lower barriers to reaction with Cl < Br < I. Our present study indicates that the isopolyhalomethanes become substantially more reactive for the O—H insertion/HX elimination reactions with methanol molecules as the halogen atoms go from I to Br to Cl with the CH_2Cl—Cl species being particularly reactive.



$(CH_2Cl\text{-}Cl) + CH_3OH \rightarrow CH_2Cl\text{-}O\text{-}CH_3 + HCl$, where SM = separated $(CH_2Cl\text{-}Cl) + CH_3OH$.



$(CH_2Br\text{-}Br) + n\ CH_3OH \rightarrow CH_2I\text{-}O\text{-}CH_3 + HBr + (n\text{-}1)\ CH_3OH$ (n=1,2,3), where SM = separated $(CH_2Br\text{-}Br) + n\ CH_3OH$.



$(CH_2I\text{-}I) + n\ CH_3OH \rightarrow CH_2I\text{-}O\text{-}CH_3 + HI + (n\text{-}1)\ CH_3OH$ (n=1,2,3), where SM = separated $(CH_2I\text{-}I) + n\ CH_3OH$.

Figure 4. Relative energy (in kcal/mol) profiles are shown for the CH_2X—X + nCH_3OH reactions obtained for the structures shown in figures 1–3 from the MP2 calculations.

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