A computational perspective on the kinetics and thermochemistry of the gas phase reactions of 1, 1-dichlorodimethylether (DCDME) with OH radical at 298 K

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A computational perspective on the kinetics and thermochemistry of the gas phase reactions of 1, 1-dichlorodimethylether (DCDME) with OH radical at 298 K

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Kinetics and thermochemistry of the gas phase reactions between CH₃OCHCl₂ (DCDME) and OH radical are investigated theoretically. The geometries and all the stationary points on the potential energy surface are calculated at BHandHLYP/6-311G(d,p) method. The energy information is further refined at CCSD(T)/6-311G(d,p) level of theory. Reaction profiles are modelled including the formation of two pre-reactive and post-complexes. The rate constants, which are evaluated by Canonical Transition State Theory (CTST) including tunnelling correction at 298 K, are in very good agreement with the available experimental data. The percentage contributions of both reaction channels are also reported at 298 K. The hydrogen abstraction reaction from the –CHCl₂ group is found to be dominant leading to the formation of CH₃OCCl₂ + H₂O. Using group-balanced isodesmic reactions, the standard enthalpies of formation for CH₃OCHCl₂, CH₃OCCl₂, CH₂OCHCl₂ and CH₂OCHCl₂ are also reported.

Keywords: hydrochloroether; rate constant; branching ratios; enthalpy of formation

Introduction

It is now a well accepted fact that the release of manmade chlorofluorocarbons (CFCs) is responsible for the depletion of ozone layer in the stratospheric region of the atmosphere [1,2]. On account of the ozone depletion caused by CFCs, global alarm was raised and serious attempts had been made in the past decade or so to find out its alternatives. Recently, hydrofluoroethers (HFEs) and hydrochloroethers (HCEs) have drawn considerable attention as third generation replacements of CFCs that may be used as cleaning agents for electronic equipments, heat transfer agents in refrigeration systems and carrier fluids for lubricant deposition [3,4]. In recent times, HCEs including DCDME have been used in the synthesis of phenalenyl-fused compounds, commercial pesticide and also some of these molecules serve as a model complex for anesthetics such as enflurane or isoflurane [5,6]. On the other hand, the HCEs contain Cl atoms and thus, the degradation products of them could be transport chlorine to the atmosphere leading to destruction of the ozone layer. Hence, there is a particular need to investigate the atmospheric chemistry of the HCEs in order to determine their atmospheric impact. It has been reported that the most likely fate of the halogenated ethers in the Earth’s atmosphere is reaction with OH radical. Therefore, considerable attention has been paid in recent years to perform experimental and theoretical studies on the decomposition kinetics of HFEs [7–14]. However, there have been fewer studies of the reactions of HCEs, as these are unlikely to be adopted for widespread use because the inclusion of chlorine would give them greater ozone-destroying potentials (ODPs). Therefore, it is important to study the kinetics and mechanistic degradation pathways of HCEs in troposphere for complete assessment of atmospheric chemistry as well as explore the significance of these substances to photochemical air pollution in metropolitan and regional areas. Dalmasso et al. [15] first experimentally studied rate constant for the reaction of DCDME with Cl atom and OH radical by using relative rate technique at 296 ± 2 K and atmospheric pressure (∼750 Torr). The experimental rate constants were derived as (CH₃OCHCl₂ + Cl) = (1.05 ± 0.11) × 10⁻¹² cm³ molecule⁻¹ s⁻¹ and (CH₃OCHCl₂ + OH) = 2.5 × 10⁻¹³ cm³ molecule⁻¹ s⁻¹, respectively. In earlier study, Dalmasso et al. [16] reported the rate constant for the same Cl atom initiated hydrogen abstraction reaction of DCDME as (1.04 ± 0.30) × 10⁻¹² cm³ molecule⁻¹ s⁻¹ at 298 ± 2 K and atmospheric pressure (750 Torr). Recently, rate constants for the gas-phase reactions of hydroxyl radicals and chlorine atoms with 2-chloroethyl methyl ether (CH₃OCH₂CH₂Cl), 2-chloroethyl ethyl ether (CH₃CH₂OCH₂CH₂Cl) and bis(2-chloroethyl) ether (CICH₂CH₂OCH₂CH₂Cl) were determined using a conventional relative rate technique at 298 ± 2 K and atmospheric pressure using synthetic air as bath gas by Dalmasso et al. [17,18]. However, experimental studies provided only the total rate constant and it is difficult to predict the detailed mechanism, thermochemistry and contribution of
each reaction channels towards overall rate constant. Thus, for better understanding of mechanistic pathways, kinetics and thermochemistry we must rely on quantum chemical methods. In the present paper, simple chloroethers were chosen as model compounds for theoretical study. Recently, we have studied the mechanism of the analogous reactions of DCDME with Cl atoms [19] considering two different reaction channels: abstraction of hydrogen from methyl (−CH₃) group or chloromethyl (−CHCl₂) group. Thus, the question arises: which is the major channel for the titled reactions? Are the reaction mechanisms similar to those of the CH₃OCHCl₂ + Cl reactions? In addition, no experimental information is available on the branching ratios of the title reactions. To the best of our knowledge, this is the first detailed theoretical study of the above-mentioned H-abstraction reactions of DCDME by OH radicals.

Our calculation indicates that in the reactant CH₃OCHCl₂ three hydrogens in the CH₃ group are equivalent, and only one channel for hydrogen abstraction is feasible. Therefore, for this molecule, two H-abstraction channels are feasible which may proceed through either from −CHCl₂ group or −CH₃ group. So the two primary processes have been considered for the title reaction as given by Rxs (R1−R2) during the present investigation.

\[
\begin{align*}
\text{CH}_3\text{OCHCl}_2 + \text{OH} &\rightarrow \text{CH}_3\text{OCCl}_2 + \text{H}_2\text{O} \quad (R1) \\
\text{CH}_3\text{OCHCl}_2 + \text{OH} &\rightarrow \text{CH}_2\text{OCHCl}_2 + \text{H}_2\text{O} \quad (R2)
\end{align*}
\]

Bond dissociation energies (BDEs) of the breaking C−H bonds are strongly correlated with the observed reactivity trend for the hydrogen abstraction reaction, and the ether linkage (−O−) is important for the reactivity of the haloethers. Thus, we present BDE of the two types of C−H and C−O bonds in CH₃OCHCl₂. In addition, the knowledge of accurate enthalpy of formation (ΔrH²⁹⁸) for CH₃OCHCl₂, CH₂OCCl₂ and CH₂OCHCl₂ is of vital importance for determining the thermodynamic properties. Here, we predict the enthalpies of formation using isodesmic reactions by performing single-point energy calculation at high level of theory, CCSD(T) with geometry parameters obtained at BHandHLYP/6-311G(d,p) level of theory. Finally, the comparison between theoretical and experimental rate constants is discussed.

**Computational methods**

Density functional and couple cluster quantum mechanical calculations were performed with the Gaussian 09 suite of programme [20]. Geometry optimisation of the reactants, products and transition states was made at the BHandHLYP [21] level of theory using 6-311G(d,p) basis set. The hybrid HF-density functional, BHandHLYP along with CCSD(T) [22] have been found to give reliable kinetics and energetic results for H-abstraction reactions [23]. The formation of pre- and post-reactive complexes along the reaction path has been observed by others for the reaction between haloethers and OH radical [11]. Two reactant complexes (RCs) and product complexes (PCs) are validated at the entrances and exits of the two H-abstraction channels, which means that the two abstraction channels may proceed via indirect mechanism. In order to determine the nature of different stationary points on the potential energy surface, vibrational frequencies were calculated using the same level of theory at which the optimisation was carried out. All the stationary points had been identified to correspond to stable minima by ascertaining that all the vibrational frequencies had real positive values. The transition states were characterised by the presence of only one imaginary frequency (NIMAG = 1). To ascertain that the identified transition states connect reactant and products smoothly, intrinsic reaction coordinate (IRC) calculations [24] were also performed at the BHandHLYP/6-311G(d,p) level. As the reaction energy barriers are very much sensitive to the theoretical levels, the higher-order correlation corrected relative energies along with the density functional energies are necessary to obtain theoretically consistent reaction energies. Therefore, a potentially high-level method such as coupled cluster [CCSD(T)] has been used for single-point energy calculations using the same basis set as mentioned above.

**Results and discussion**

The calculated enthalpy of reactions (ΔrH°), reaction free energies (ΔrG°) and Gibbs free energy of activation (ΔG°) at 298 K for the reaction of CH₃OCHCl₂ with OH radical are recorded in Table 1. A free energy value shows that both reaction channels are exergonic (ΔG° < 0). The enthalpy of reaction (ΔrH₂⁹⁸°) values tabulated in Table 1 for R1 and R2 show that both the reactions are significantly exothermic in nature and thus thermodynamic facile. The ΔrH°₂⁹⁸ values obtained from the CCSD(T) and BHandHLYP methods for R1 and R2 at 298 K differ by almost 2.9 kcal mol⁻¹. Moreover, reaction R1 is more exothermic than the R2 by about 3.6 kcal mol⁻¹. Thus, R1 may be thermodynamically more favourable than R2, and the rate constant of R1 will be faster than R2. Since the three H atoms in −CH₃ group are equivalent, only one transition channel is considered.

<table>
<thead>
<tr>
<th>Reaction channels</th>
<th>ΔrH°</th>
<th>ΔrG°</th>
<th>ΔG°</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>−15.85 (−18.24)</td>
<td>−17.20 (−19.60)</td>
<td>10.75 (8.01)</td>
</tr>
<tr>
<td>R2</td>
<td>−11.57 (−14.42)</td>
<td>−12.66 (−15.51)</td>
<td>13.08 (10.90)</td>
</tr>
</tbody>
</table>
state is located for reaction channel R1. The optimised geometries with some structural parameters obtained at BHandHLYP/6-311G(d,p) level for reactants (CH₃OCHCl₂ and OH), reaction complexes (RC1 and RC2), transition states (TS1 and TS2), products complexes (PC1 and PC2) and products (CH₂OCCl₂, CH₂OCHCl₂ and H₂O) involved in the reactions (R1–R2) are given in Figure 1 with available limited experimental values. The data shown in Figure 1 reveal that the calculated bond distances for OH and H₂O are in very good agreement with the corresponding experimental values [25]. The bond distance between the hydrogen atom in CH₃OCHCl₂ and oxygen atom of the hydroxyl radical in RC1 and RC2 are 2.74 and 2.38 Å, respectively while the other bonds are similar to the reactant.

During the formation of transition states, the important structural parameters have to be observed are one of the C–H bond of the leaving hydrogen and the newly formed bond between H and O atoms in the OH radical. From
Table 2. Unscaled vibrational frequencies of reactants, products and transition states at BHandHLYP/6-311G(d,p) level of theory.

<table>
<thead>
<tr>
<th>Species</th>
<th>Vibrational frequencies (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_3)OCH(_2)Cl</td>
<td>103, 182, 265, 286, 424, 445, 724, 855, 1050, 1206, 1222, 1278, 1326, 1411, 1538, 1543, 1559, 3108, 3184, 3202, 3247</td>
</tr>
<tr>
<td>RC1</td>
<td>30, 60, 114, 123, 187, 223, 267, 287, 400, 425, 451, 742, 849, 1041, 1191, 121, 1274, 1326, 1409, 1536, 1547, 1555, 3121, 3199, 3233, 3247, 3682</td>
</tr>
<tr>
<td>TS1</td>
<td>1630i, 95, 112, 126, 191, 201, 261, 290, 393, 432, 513, 773, 811, 925, 1042, 1213, 1225, 1288, 1328, 1457, 1539, 1544, 1562, 3136, 3218, 3256, 3910</td>
</tr>
<tr>
<td>PC2</td>
<td>33, 77, 106, 136, 156, 199, 242, 279, 293, 335, 437, 450, 728, 734, 859, 1059, 1242, 1303, 1367, 1441, 1529, 1678, 3224, 3251, 3370, 3954, 4057</td>
</tr>
<tr>
<td>CH(_3)OCCl(_2)</td>
<td>77, 168, 243, 291, 437, 470, 621, 919, 1049, 1216, 1238, 1316, 1539, 1544, 1555, 3136, 3215, 3255</td>
</tr>
<tr>
<td>CH(_2)OCH(_2)Cl</td>
<td>100, 213, 278, 290, 431, 448, 649, 739, 859, 1072, 1232, 1298, 1333, 1409, 1528, 3226, 3231, 3382</td>
</tr>
<tr>
<td>OH</td>
<td>3892</td>
</tr>
<tr>
<td>H(_2)O</td>
<td>1688, 3988, 4089</td>
</tr>
</tbody>
</table>

In Figure 1, we can predict that in the optimised structure of TS1, the length of the breaking C–H bond (C2–H3) increases from 1.080 to 1.190 Å (almost an 10% increase) whereas the newly formed H–O bond (H3–O3) is increased from 0.967 to 1.303 Å resulting in an increase of about 35%. The fact that the elongation of forming bond is larger than that of the breaking bond indicates that the barrier of the reaction is near the corresponding reactants. This means the reaction will proceed via early transition state structure which is in consonance with Hammond’s postulate [26] applied to an exothermic hydrogen abstraction reaction. While for the transition state (TS2), the length of the breaking C–H bond (C1–H1) increases from 1.080 to 1.246 Å (almost 15% increase) whereas the newly formed H–O bond (H1–O2) is increased from 0.967 to 1.282 Å resulting in an increase of about 32%. It indicates that the barrier of this reaction (R2) lies near the reactant and the reaction with OH radical will proceed via an early transition state which is consistent with Hammond’s postulate applied to an exothermic reaction [26]. Results obtained during frequency calculations for species involved in reactions (R1) and (R2) are recorded in Table 2. These results show that all the reactants, products and complexes have stable minima on their potential energy surface characterised by the occurrence of only real positive vibrational frequencies. The transition states are confirmed by normal mode analysis to have only one imaginary frequency which takes the values of 1630i (TS1) and 1744i (TS2), respectively. Visualisation of the vibration corresponding to the calculated imaginary frequencies using ChemCraft [27] programme shows a well defined transition state geometry connecting reactants and products during transition. The existence of transition state on the potential energy surface is further ascertained by intrinsic reaction coordinate (IRC) calculation performed at the same level of theory using the Gonzalez–Schlegel steepest descent path in the mass-weighted Cartesian coordinates with a step size of 0.01 (amu\(^{1/2}\)-bohr) [24]. The IRC plots for TS1 and TS2 clearly authenticate a smooth transition from reactants to products along the potential energy surface.

Single point energy calculations of various species involved in the hydrogen abstraction reactions were further refined by using coupled cluster [CCSD(T)] level of theory at BHandHLYP/6-311G(d,p) optimised geometries. The relative energies (including ZPE) for all the species involved in reactions R1 and R2 are presented in Table 3. A schematic diagram of the potential energy surface for the reaction CH\(_3\)OCH\(_2\)Cl + OH is shown in Figure 2. In the construction of energy diagram, the ground state energies of the reactants are arbitrarily taken as zero. The values in parentheses are calculated at BHandHLYP/6-311G(d,p) level. The CCSD(T) calculated barrier heights for hydrogen abstrac-

Table 3. Relative energies of the species at BHandHLYP/6-311G(d,p) and CCSD(T)/6-311G(d,p) level of theories including zero-point energy (ZPE) correction estimated at BHandHLYP/6-311G(d,p) level. All values are in kcal mol\(^{-1}\).

<table>
<thead>
<tr>
<th>Species</th>
<th>BHandHLYP</th>
<th>CCSD(T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_3)OCH(_2)Cl + OH</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>RC1</td>
<td>−0.85</td>
<td>−1.31</td>
</tr>
<tr>
<td>RC2</td>
<td>0.52</td>
<td>0.97</td>
</tr>
<tr>
<td>TS1</td>
<td>5.54</td>
<td>2.78</td>
</tr>
<tr>
<td>TS2</td>
<td>8.19</td>
<td>5.82</td>
</tr>
<tr>
<td>PC1</td>
<td>−16.97</td>
<td>−19.66</td>
</tr>
<tr>
<td>PC2</td>
<td>−12.74</td>
<td>−15.66</td>
</tr>
<tr>
<td>CH(_3)OCCl(_2) + H(_2)O</td>
<td>−13.06</td>
<td>−15.45</td>
</tr>
<tr>
<td>CH(_3)OCH(_2)Cl + H(_2)O</td>
<td>−8.75</td>
<td>−11.60</td>
</tr>
</tbody>
</table>
tion from the –CHCl₂ (R1) and –CH₃ (R2) are 2.78 and 5.54 kcal mol⁻¹, respectively, whereas these values are 5.82 and 8.19 kcal mol⁻¹, respectively at BHandHLYP level. It shows that hydrogen abstraction from the –CHCl₂ group is more favourable than that from the –CH₃ group. Literature survey reveals that there is no experimental data available for the comparison of the energy barrier for the H-atom abstraction reaction of CH₃OCHCl₂ by OH radical. Moreover, our single configuration quantum mechanical calculations are likely to be reliable, since spin contamination is not important for the CH₃OCHCl₂ because <S²> is found to be 0.76 at BHandHLYP/6-311G(d,p) before annihilation that is only slightly larger than the expected value of <S²> = 0.75 for doublets.

The calculated BDEs (D₀²⁹₈) of the C–H and C–O bonds in CH₃OCHCl₂ at CCSD(T) level are listed in Table 4. Our calculated D₀²⁹₈ (C–H) values obtained at CCSD(T) level in –CHCl₂ and –CH₃ group of CH₃OCHCl₂ are 99.93 and 103.72 kcal mol⁻¹, respectively. Thus, it is expected that hydrogen abstraction to be mainly from the –CHCl₂ site of the CH₃OCHCl₂ molecule. The change in BDE is also in line with the change of barrier heights mentioned earlier. At the same level, the D₀²⁹₈ (C–O) values obtained from the two pathways are 90.96 and 90.11 kcal mol⁻¹. Since, the D₀²⁹₈ values of C–O bonds are lower than that of two types of C–H bonds, the broken of C–O bond may play an important role for the CH₃OCHCl₂ at stratospheric level. No comparison between theory and experiment can be made due to the lack of the experimental D₀²⁹₈ (C–O) values. In order to check accuracy of the calculations, the value of BDE of the O–H bond in the water molecule has been computed and compared to the literature data. The experimental value of D₀²⁹₈ of the O–H bond in water is 119.0 kcal mol⁻¹ [28]. D₀²⁹₈ calculated at the CCSD(T)//BHandHLYP/6-311G(d,p) level, in this work, is 119.2 kcal mol⁻¹. Thus, the value of D₀²⁹₈ of the O–H bond in water, obtained at the theoretical level applied in this work, almost reproduces the experimental value. The good agreement between the theoretical and experimental above-mentioned result implies that the CCSD(T)//BHandHLYP/6-311G(d,p) level is a suitable method to compute the bond dissociation energies and our calculated D₀²⁹₈ (C–H) and D₀²⁹₈ (C–O) values may be expected to provide reliable reference information for future laboratory investigations.

The standard enthalpy of formation (ΔH₂⁹₈) at 298 K for CH₃OCHCl₂ and the radical generated from hydrogen abstraction, CH₃OCCl₂ and CH₃OCHCl₂ can be valuable information for understanding thermochemical properties of their reactions and most importantly for atmospheric modelling, but these values are not yet reported. The group-balanced isodesmic reactions, in which the number and types of bonds are conserved, are used as working chemical reactions herein to calculate the ΔH₂⁹₈ for CH₃OCHCl₂. Here, three isodesmic reactions [29] for CH₃OCHCl₂ and radicals generated by hydrogen abstraction are used to estimate the enthalpies of formation of the species. The used isodesmic reactions (R3–R11) are as follows:

(a) CH₃OCHCl₂

CH₃OCHCl₂ + CH₄ → CH₃OCH₃ + CH₂Cl₂ (R3)

(b) CH₃OCCl₂

CH₃OCCl₂ + CH₄ → CH₃OCH₃ + CHCl₂ (R6)

CH₃OCCl₂ + CH₄ → CH₃OCHCl₂ + CH₃ (R7)

<table>
<thead>
<tr>
<th>Bond dissociation type</th>
<th>Energy (kcal mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>C–H bond</strong></td>
<td></td>
</tr>
<tr>
<td>CH₃OCHCl₂ → CH₃OCCl₂ + H</td>
<td>99.93</td>
</tr>
<tr>
<td>CH₃OCHCl₂ → CH₂OCHCl₂ + H</td>
<td>103.72</td>
</tr>
<tr>
<td><strong>C–O bond</strong></td>
<td></td>
</tr>
<tr>
<td>CH₃OCHCl₂ → CH₂O + CHCl₂</td>
<td>90.96</td>
</tr>
<tr>
<td>H₂O → HO + H</td>
<td>119.1 (119.0)</td>
</tr>
</tbody>
</table>

*Experimental value from Lide [28].
(c) CH₂OCHCl₂
CH₂OCHCl₂ + CH₂Cl₂ → CH₂OCHCl₂ + CHCl₂ (R9)

CH₂OCHCl₂ + CH₄ → CH₂OCH₃ + CHCl₂ (R10)
CH₂OCHCl₂ + CH₄ + H₂O → CH₃OH + CH₂OH + CHCl₂ (R11)

All geometrical parameters of the species involved in the isodesmic reactions (R3–R11) are calculated at the BHandHLYP/6-311G(d,p) level and energies of the species are refined at the CCSD(T)/6-311G(dp) levels of theory. The optimised geometries and the structural parameters obtained at BHandHLYP/6-311G(dp) level for species involved in the reactions (R3–R11) are given in Table S1–S11 in supplementary material. The calculated total energies and ZPE corrections for all the species involved in isodesmic reactions R3–R11 are given in Table S12 in supplementary material. Since, the (ΔfH°298) values correspond to the difference of the enthalpy of formation (ΔfH°298) values between the products and the reactants, the (ΔfH°298) values of the reactant and product species are easily evaluated by combining them with the known enthalpies of formation of the reference compounds involved in our isodesmic reaction schemes. (CH₄: −17.89 kcal mol⁻¹ [30], CH₂OCH₃: −44.0 kcal mol⁻¹ [31], CF₂Cl₂: −117.72 kcal mol⁻¹ [32], CH₂F₂: −107.81 kcal mol⁻¹ [30], CH₃OH: −48.08 kcal mol⁻¹ [33], H₂O: −57.80 kcal mol⁻¹ [30] and CH₂Cl₂: −22.83 kcal mol⁻¹ [34], CHCl₂: 23.5 kcal mol⁻¹ [34], and CH₃: 34.82 kcal mol⁻¹ [30].)

For example, (ΔfH°298) of CH₂OCHCl₂ are calculated from the isodesmic reaction R3 as follows:

$$
\Delta fH°^{298}(R3) = \Delta fH°^{298}(\text{CH₂OCH₃}) + \Delta fH°^{298}(\text{CH₂Cl₂}) - \Delta fH°^{298}(\text{CH₂OCHCl₂}) - \Delta fH°^{298}(\text{CH₄})
$$

The calculated reaction enthalpies (ΔfH°298) of all isodesmic reactions (R3–R11) and enthalpies of formation (ΔfH°298) of species are listed in Table 5. As can be seen from Table 5, the values of ΔfH°298 for the species obtained by the three working chemical reactions are reasonably consistent with each other. Moreover, because of the lack of the experimental values for the ΔfH°298 of the great majority of the species involved in the title reactions, it is difficult to make a direct comparison between theoretical and experimental enthalpy of formation. However, it is seen that our calculated ΔfH°298 value for CH₂OCHCl₂ (−62.45 kcal mol⁻¹) at CCSD(T)/BHandHLYP/6-311G(dp) level is well consistent with the recommended value of −62.28 ± 2.10 kcal mol⁻¹ for CH₂OCHCl₂ at CBS-QB3/B3LYP/6-31G(dp) level by Jung and Bozzelli [35].

<table>
<thead>
<tr>
<th>Species</th>
<th>Reaction enthalpy (ΔfH°298)</th>
<th>ΔfH°298 at 298°C</th>
<th>Average value of Literature</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₂OCHCl₂</td>
<td>R3 13.73</td>
<td>−62.67</td>
<td>−62.28*</td>
</tr>
<tr>
<td>CH₂OCCl₂</td>
<td>R6 11.89</td>
<td>−14.50</td>
<td>—</td>
</tr>
<tr>
<td>CH₂OCHCl₂</td>
<td>R9 −5.69</td>
<td>−10.42</td>
<td>—</td>
</tr>
<tr>
<td>CH₂OCHCl₂</td>
<td>R10 8.035</td>
<td>−10.64</td>
<td>−10.38</td>
</tr>
<tr>
<td>R11 13.13</td>
<td></td>
<td>−10.10</td>
<td></td>
</tr>
</tbody>
</table>

*From ref. [35].

This infers that the ΔfH°298 values obtained for radical species, CH₃OCCl₂ (−14.65 kcal mol⁻¹) and CH₂OCHCl₂ (−10.38 kcal mol⁻¹) at CCSD(T)/BHandHLYP/6-311G(dp) level are also reliable. The slightly lower value of ΔfH°298 for CH₃OCCl₂ compared to CH₂OCHCl₂ suggests that this product is more stable.

### Rate constants and branching ratios

The rate constant for hydrogen abstraction reactions was estimated using Canonical Transition State Theory (CTST) [36] that involves a semi-classical one-dimensional multiplicative tunnelling correction factor given by the following expression:

$$
k = \sigma \Gamma(T) \frac{k_B T}{h} \frac{Q^\dagger}{Q_R} \exp \left( -\frac{\Delta E}{k_B T} \right),
$$

where σ is reaction degeneracy, Q^\dagger, and Q_R are the total partition functions (per unit volume) for the transition states and reactants, respectively, ΔE is the barrier height including zero-point energy correction, k_B is the Boltzmann constant and h is the Plank’s constant. R represents the universal gas constant. The Γ(T) tunnelling correction factor at temperature T was estimated by using Wigner’s method [37] using the expression

$$
\Gamma(T) = 1 + \frac{1}{24} \left( \frac{h \nu^\dagger}{k_B T} \right)^2,
$$

where ν^\dagger is the imaginary frequency at the saddle point. The partition functions for the respective transition states and reactants at 298 K are obtained from the vibrational frequencies calculation made at BHandHLYP/6-311G(dp) level. Most of the vibrational modes were treated as quantum-mechanical harmonic oscillators. The hindered-rotor approximation of Truhlar and Chuang [38] was used for...
calculating the partition function of lower vibration modes. The branching ratios for the two H-abstraction reaction channels, which represent their individual contribution towards overall reaction rate, have been determined by using the following expression

$$\Gamma_{1/2} = \frac{k_{1/2}}{k_{\text{total}}} \times 100.$$  \hspace{1cm} (R14)

The partial rate coefficients cannot be determined experimentally because reactions occur simultaneously, and in some cases they even lead to the same products. Thus, the experimental data are mostly available only for the overall reactions. That is why theoretical methods can be so valuable for the full understanding of the chemical systems, provided that they have previously proved their reliability. The comparison between experimental and calculated overall data is in most cases the only available criterion for that purpose. The CTST coupled with Wigner’s tunnelling methods was used previously in earlier reports to compute rate constant for hydrogen abstraction reactions [39–43]. The agreement between the theoretically calculated rate constant with OH radicals using the above said methods was found to be in good agreement with the experimental findings. It has been observed that H-abstraction by OH radical proceeds via two-step mechanism. The first step involves a formation of the pre-reactive complexes (RCs) with pre-equilibrium rate constant (Keq) and the second step yielding the corresponding radical and water with the rate constant \(k_2\). The overall rate constant including equilibrium constant (Keq) and rate constant (\(k_2\)) are given by

$$K_{\text{eq}} = \frac{Q_{\text{RC}}}{Q_R} e^{(E_R - E_{\text{RC}})/RT}.$$  \hspace{1cm} (R15)

and \(k_2\) can be obtained from TST in the form

$$k_2 = \Gamma(T) \sigma \frac{k_BT}{h} \frac{Q_{\text{TS}}}{Q_R} e^{-(E_{\text{TS}} - E_{\text{RC}})/RT}.$$  \hspace{1cm} (R16)

The rate constant for H-abstraction from DCDME via reactions (R1–R2) is then obtained by the following expression

$$K = K_{\text{eq}} \times k_2 = \Gamma(T) \sigma \frac{k_BT}{h} \frac{Q_{\text{TS}}}{Q_R} e^{-(E_{\text{TS}} - E_R)/RT}.$$  \hspace{1cm} (R17)

Thus it seems that the final expression (Equation (R17)) for estimating rate constant and barrier height turns out to be the usual CTST expression (Equation (R12)) used for the determination of rate constant and barrier height of a direct reaction, irrespective of the energy of pre-reactive reactant complexes (RC1 and RC2). However, the formation of pre- and post-reaction complex affects the tunnelling factor by modifying the shape of the potential energy surface. Thus, the rate constant for hydrogen abstraction reaction also changes significantly. During the calculation of the rate constant, vibrational partition functions were considered from first ground vibrational level. The translational partition function was evaluated per unit volume. Electronic partition function for OH radical was evaluated by considering the splitting of 140 cm\(^{-1}\) in the \(2\Pi\) ground state into account. The total partition function was calculated as a product of the individual partition functions, the translational, rotational, vibrational and electronic partition functions. All these partition functions for the respective transition states, reaction complexes and reactants at 298 K are obtained from the Gaussian output during vibrational frequencies calculation estimated at BHandHLYP/6-311G(d,p) level. Energy barrier of reactants, reaction complexes and transition states calculated at CCSD(T)/6-311G(d,p) level as shown in Table 3 are considered throughout our rate constant calculation using CTST. The tunnelling correction factors \(\Gamma(T)\) calculated by using one-dimensional Wigner’s method are found to be 3.57 and 3.95, respectively for TS1 and TS2. The calculated rate constants for H atom abstraction reactions from –CHCl\(_2\) and –CH\(_3\) groups as given by reactions (R1–R2) are found to be 1.95 \(\times\) \(10^{-13}\) and 8.78 \(\times\) \(10^{-15}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\), respectively at 298 K. It has been assumed that neither mixing nor crossover between different pathways occurs. Thus, the overall rate constant corresponding to CH\(_2\)OCHCl\(_2\) + OH can be determined as the sum of the rate coefficients of each reaction channel. The calculated overall rate constant (2.03 \(\times\) \(10^{-13}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\)) at 298 K is in very good agreement with the available experimental value of (2.5 \(\times\) \(10^{-13}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) \(\pm\) 0.2) reported by Dalmasso et al. [15]. Therefore, the good agreement between experimental and calculated (overall) results obtained in this work supports the quality of the kinetic data obtained in this present work. This good agreement also justifies the use of the partial rate constants (corresponding to each independent channel) in the study of the reasons which can cause the peculiar reactivity in chloroethers + OH reactions. The calculated branching ratios for reactions (R1–R2) as 96.0% and 4.0%, respectively at 298 K clearly indicate that H-abstraction from –CHCl\(_2\) sites makes the largest contribution to the overall rate constant compared to its –CH\(_3\) counterpart.

Conclusions

The hydrogen abstraction reaction from DCDME with OH radical has been presented by a complex mechanism involving the formation of two reactant complexes in the entrance channel and two product complexes in the exit channel. The potential energy surface and reaction kinetics for the indirect mechanism are investigated at CCSD(T)//BHandHLYP/6-311G(d,p) level of theory. The barrier heights for reaction pathways (R1) and (R2) calculated at CCSD(T) level are found to be 2.78 and 5.82 kcal mol\(^{-1}\), respectively. The thermal rate constant is found to be
2.03 × 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) at 298 K which is in good agreement with available experimental data. The branching ratio calculations suggest that the H abstraction from –CHCl₂ site is more favourable than the methyl group. The ΔH^\circ_{298} values for CH₃OCHCl₂, CH₃OCCl₂, and CH₂OCHCl₂ are predicted to be \(-62.45, -14.65\) and \(-10.38 \text{ kcal mol}^{-1}\), respectively.

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Supplemental data

Supplemental data for this article can be accessed here.

References