

## The CH<sub>3</sub>OH+Cl Hydrogen Abstraction Reactions: An *ab initio* Study

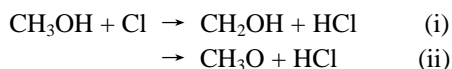
Bo Zhen CHEN, Ming Bao HUANG\*

Graduate School, Academia Sinica, Beijing 100039

**Abstract:** The two channels of the CH<sub>3</sub>OH+Cl hydrogen abstraction reaction, leading to the final products CH<sub>2</sub>OH+HCl (i) and CH<sub>3</sub>O+HCl (ii), have been studied by performing *ab initio* MP2 calculations with the triplet split-valence polarization basis sets. For each of the two channels the following simple reaction path is predicted: reactants → transition state → intermediate → products. The previously reported complicated paths<sup>2</sup> calculated without using the IRC technique are criticized. Our calculations indicate that channel (i) is exothermic and has a negligible energy barrier while channel (ii) is endothermic and has a substantial energy barrier. These results imply that channel (i) is favorable, which is in line with experiment.

**Keywords:** Abstraction reaction, *ab initio* calculation, IRC.

The hydrogen abstraction from methanol by atomic chlorine can proceed *via* two possible channels:



In 2000, Ahmed *et al*<sup>1</sup>. reported their investigation for the H abstraction dynamics of the CH<sub>3</sub>OH+Cl reaction by crossed molecular beams in conjunction with velocity map imaging. Hydroxymethyl (CH<sub>2</sub>OH) was detected in their experiments. In 1998, Jodkowski *et al*<sup>2</sup>. reported their theoretical study on the CH<sub>3</sub>OH+Cl reactions. They located intermediate complexes and transition states by performing the MP2/6-311G (d,p) calculations and presented a “reaction path” diagram for the CH<sub>3</sub>OH+Cl hydrogen abstraction reactions<sup>2</sup>. As pointed out by Ahmed *et al*<sup>1</sup>., the reaction paths were not explicitly considered in the work of Jodkowski *et al*<sup>2</sup>., and we also note that they did not carry out IRC (intrinsic reaction coordinate) calculations.

We recently studied the CH<sub>3</sub>OH+Cl hydrogen abstraction reactions [channels (i) and (ii)] by performing *ab initio* (U)MP2 [(unrestricted) second-order Moller-Plesset perturbation theory<sup>3</sup>] calculations, and the reaction path calculations included geometry optimization and frequency analysis calculations followed by the important IRC calculations.

The (U)MP2 calculations were carried out with the Gaussian 94W Suite of programs<sup>4</sup> and the basis sets used were 6-311G (d,p), 6-311+G (d,p), 6-311++G (d,p), and 6-311++G (2d,p)<sup>5</sup>. The MP2 geometry optimization calculations with the 6-311G (d,p), 6-311+G (d,p), and 6-311++G (d,p) basis sets were performed for locating the stationary points along the reaction paths, and the MP2 frequency analysis calculations with the same three basis sets were performed for characterizing stationary points as

intermediate complexes (IMs) or transition states (TSs) and evaluating zero point energies (ZPEs). In order to check the reaction paths, we carried out the IRC calculations starting at transition states at the MP2/6-311G (d, p) level. For IM1 and IM2, we also carried out geometry optimization calculations at the MP2/6-311++G (2d,p) level. All the MP2 calculations were carried out with core orbitals frozen. In the UMP2 calculations for open-shell systems, the  $\langle S^2 \rangle$  values are smaller than 0.784 and the spin-projected energetic results are used.

The potential energy curves shown in **Scheme** represent schematically the calculated reaction paths for channels (i) and (ii) of the CH<sub>3</sub>OH+Cl hydrogen abstraction reaction, and the values given in **Scheme** are the MP2/6-311++G (d, p) relative energies of TSs, IMs, and the final products to the reactants. In **Table 1** given are the MP2/6-311G (d, p), MP2/6-311+G (d, p), and MP2/6-311++G (d, p) relative energies, together with the MP2/6-311++G (d, p) ZPEs. The energetic results indicate that the MP2 calculations with the three basis sets predict the same skeleton (see **Scheme**) of the energy profile for each of the two channels. In the following discussion the MP2/6-311++G (d, p) relative energies are used.

**Table 1** Relative energies (kcal/mol) of TSs, IMs, and products for channels (i) and (ii) of the CH<sub>3</sub>OH+Cl hydrogen abstraction reaction, together with the MP2/6-311++G(d,p) ZPEs (kcal/mol).

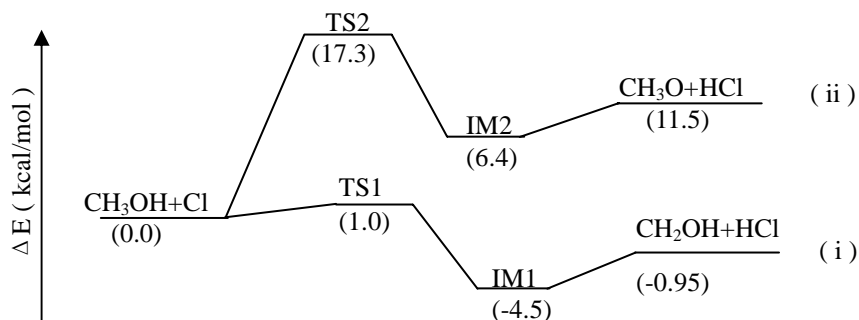
	MP2/6-311G (d, p)	MP2/6-311+G (d, p)	MP2/6-311++G (d, p)	ZPE
CH <sub>3</sub> OH+Cl	0.0	0.0	0.0	32.7
TS1	1.2	1.2	1.0	30.6
IM1	-5.0	-4.3	-4.5	29.7
CH <sub>2</sub> OH+HCl	-1.4	-0.84	-0.95	28.4
TS2	15.8	17.5	17.3	28.3
IM2	4.2	6.6	6.4	29.7
CH <sub>3</sub> O+HCl	10.0	11.6	11.5	28.1

The reaction process for channel (i) consists of two steps: (1) attack of the Cl atom on a methyl hydrogen leading to an intermediate IM1 *via* a transition state TS1; and (2) dissociation of IM1 into CH<sub>2</sub>OH+HCl with no energy barrier. The relative energies of TS1 and IM1 are predicted to be 1.0 and -4.5 kcal/mol, respectively (the ZPE-corrected relative energies being -1.1 and -7.5 kcal/mol, respectively). The relative energy of -5.3 kcal/mol (with the ZPE corrections) for CH<sub>2</sub>OH+HCl is comparable with the experimental  $\Delta H$  value of  $-6.8 \pm 1.0$  kcal/mol<sup>6</sup> for the CH<sub>3</sub>OH+Cl  $\rightarrow$  CH<sub>2</sub>OH+HCl reaction. Our calculations indicate that channel (i) of the CH<sub>3</sub>OH+Cl hydrogen abstraction reaction is exothermic and has a negligible energy barrier.

The reaction process for channel (ii) also consists of two steps: (1) attack of the Cl atom on the hydroxyl hydrogen leading to IM2 *via* TS2; and (2) dissociation of IM2 into CH<sub>3</sub>O+HCl with no energy barrier. The relative energies of TS2 and IM2 are predicted to be 17.3 and 6.4 kcal/mol, respectively (the ZPE-corrected relative energies being 12.9 and 3.4 kcal/mol, respectively). The relative energy of 6.9 kcal/mol (with the ZPE corrections) for CH<sub>3</sub>O+HCl is in reasonable agreement with the experimental  $\Delta H$  value of  $2.3 \pm 1.0$  kcal/mol<sup>6</sup> for the CH<sub>3</sub>OH+Cl  $\rightarrow$  CH<sub>3</sub>O+HCl reaction. Our calculations indicate that channel (ii) of the CH<sub>3</sub>OH+Cl hydrogen abstraction reaction is endothermic and has a substantial energy barrier. Our calculation results for both the

channels imply that channel (i) is favorable, which is in line with experiment<sup>1</sup>.

**Scheme** A schematic diagram of the potential energy curves for channels (i) and (ii) of the CH<sub>3</sub>OH+Cl hydrogen abstraction reactions (the values are the MP2/6-311++G (d,p) relative energies ).



It is noted that our calculated reaction paths (shown in **Scheme**) for channels (i) and (ii) of the CH<sub>3</sub>OH+Cl hydrogen abstraction reactions are completely different from those complicated paths reported by Jodkowski *et al.*<sup>2</sup> (shown in **Figure 3** of Ref.2). Based on our calculations, their intermediates “MC2” and “MC3” do not exist along the reaction paths. The transition state along their reaction path for channel (ii) was linked to three minimum-energy stationary points, which is apparently wrong (they did not carry out IRC calculations !).

The structures of CH<sub>2</sub>OH, TS1, IM1, and IM2 are predicted to have the C<sub>1</sub>-symmetry, while those of CH<sub>3</sub>OH, CH<sub>3</sub>O, and TS2 to have the C<sub>s</sub>-symmetry. In the MP2 calculations with the 6-311G (d, p), 6-311+G (d, p), and 6-311++G (d, p) basis sets, the (Cl)H-C bond distance in IM1 is predicted to be 2.240, 2.220, and 2.165 Å, and the (Cl)H-O bond distance in IM2 to be 1.971, 1.963, and 1.947 Å, respectively. Considering these long lengths of the linkage bonds and the small values of the dissociation energies (evaluated using the energies of the intermediates and the final products given in **Table 1**) for IM1 and IM2, one may suspect that in the calculations of higher levels IM1 and IM2 would disappear (namely, the two reaction channels would become one-step reactions). However, in the MP2 calculations using a 6-311++G (2d, p) basis set, we located the IM1 and IM2 structures (the predicted linkage bond distances being 2.137 Å and 1.934 Å, respectively). In the DFT B3LYP calculations with the 6-311G (d, p), 6-311+G (d, p), and 6-311++G (d, p) basis sets, we also located the IM1 and IM2 structures (the predicted linkage bond distances being 1.852-1.914 Å for IM1 and 1.845-1.880 Å for IM2).

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**Erratum:** The author's name in CCL Vol. 12 (06), p. 489, Ru Ru CHEN should be corrected to Ru Yu CHEN