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Quantum Monte Carlo study of the reaction: $Cl + CH_3OH \rightarrow CH_2OH + HCl$

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Abstract

A theoretical study is reported of the $Cl+CH_3OH \rightarrow CH_2OH + HCl$ reaction based on the diffusion Monte Carlo (DMC) variant of the quantum Monte Carlo method. Using a DMC trial function constructed as a product of Hartree-Fock and correlation functions, we have computed the barrier height, heat of reaction, atomization energies and heats of formation of reagents and products. The DMC heat of reaction, atomization energies, and heats of formation are found to agree with experiment to within the error bounds of computation and experiment. Moller-Plesset second order perturbation theory (MP2) and density functional theory, the latter in the B3LYP generalized gradient approximation, are found to overestimate the experimental heat of reaction. Intrinsic reaction coordinate calculations at the MP2 level of theory demonstrate that the reaction is predominantly direct, i.e., proceeds without formation of intermediates, which is consistent with a recent molecular beam experiment. The reaction barrier as determined from MP2 calculations is found to be 2.24 kcal/mol and by DMC it is computed to be 2.39(49) kcal/mol.

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I. Introduction

Abstraction reactions of hydrogen atoms from alcohols, ethers, and hydrocarbons are of great importance in combustion,[1] atmospheric science,[2] and surface chemistry.[3] Radical species such as CH_3O and CH_2OH are believed to play a significant role as intermediates in the combustion of hydrocarbon fuels[4] and atmospheric reactions.

The abstraction of hydrogen from methanol by Cl has been studied recently in a crossed molecular beam (CMB) that used velocity map imaging,[5,6] in a bulb experiment that used 2+1 resonance enhanced multiphoton ionization (REMPI) with a time of flight mass spectrometer (TOF MS)[7], and in chemical kinetics experiments.[8] The nucleophilic reaction of a chlorine atom with methanol yields hydroxymethyl radical and hydrogen chloride[5] i.e.,

$$Cl+CH_3OH \rightarrow \cdot CH_2OH+HCl \quad \Delta H_{rx}^{298K} = -6.8 \text{ kcal/mol}^{9} \tag{1}$$

The rate coefficients and energetics of Eq. (1) are well established.[7] The abstraction by Cl of a methyl group H to form hydroxymethyl radical has been reported to be the dominant reaction pathway (~95%) with a moderately fast reaction rate of $5.3 - 6.3\times10^{-11}$ $cm^3molecule^{-1}s^{-1}$ with no appreciable barrier.[8,10]

In the present study, the heat of reaction and transition state are examined using the diffusion Monte Carlo (DMC) method while the reaction path is calculated using Moller-Plesset second order perturbation theory (MP2). This study is motivated by recent CMB with velocity map imaging experiments of Ahmed *et al*.,[5,6] at 8.7 kcal/mol collision energy which showed strong evidence of direct reaction. The observed distribution is predominantly backscattered which is indicative of a direct process. In the experiment 30-40% of the available energy is released as product translation. Significant

contribution of long-lived complexes was ruled out due to the asymmetry of the differential cross section.

A detailed *ab initio* theoretical study by Jodkowski *et al*.[9] proposed a reaction pathway that proceeds through formation of molecular complexes. The authors carried out MP2 and Gaussian-2 (G2) computations,[11] with a variety of basis sets, at several points on the potential energy surface (PES).

More recent REMPI/TOF MS experiments by Rudic *et al*.[7] at 5.6 kcal/mol collision energy support CMB's finding that the reaction occurs through a different mechanism than that proposed by Jodkowski *et al*.[9] Although the REMPI/TOF MS and the CMB experiments were carried out at different mean collision energies, Rudic *et al.*, report that the dynamics of the experiments are similar.[7]

Intrinsic reaction coordinate (IRC) calculations were reported by Chen and Huang[12] at the MP2 and density functional theory (DFT) in the B3LYP generalized gradient approximation (GGA) levels of theory with various basis sets. These authors found a small barrier to the reaction in accord with Jodkowski *et al.*[9]

In this paper, we report the heat of reaction for $Cl + CH_3OH \rightarrow HCl + CH_2OH$. In addition we present the heats of formation and atomization energies of the ground states of HCl, CH_3OH, and CH_2OH; a preliminary account of this study has appeared elsewhere.[13] All of the aforementioned quantities were computed using the DMC method and Hartree-Fock (HF) trial functions. The atomic cores were described with the Stevens Basch Krauss (SBK)[14] effective core potentials (ECP) while the cc-pVTZ basis set[15] was used to describe the valence electrons. For comparison, MP2 and B3LYP computations were carried out and the results are reported below. Further an IRC at the MP2/6-

311++G** level of theory was calculated in this study and found to be similar to the IRC of Chen and Huang.[12]

The remainder of the paper is organized as follows. Section II summarizes the DMC method and describes the trial wave functions used for the DMC calculations. In Sec. III, atomization energies, heats of formation, the heat of reaction, and the reaction barrier height are reported and discussed. Section IV summarizes results and presents conclusions.

II. Method

The DMC approach is a stochastic method for obtaining time independent solutions to the Schrödinger equation by solving the time-dependent Schrödinger equation in imaginary time.[16] The solution of the latter equation converges to the overall bosonic ground state.[17] Fermion antisymmetry is introduced through the fixed-node approximation (FNA),[18] which imposes the nodes of an approximate wave function Ψ_T onto the unknown exact wave function Φ.[19] The FNA has been found to provide accurate results for ground and excited states with trial functions constructed using various ab initio basis set methods.[20] The introduction of information on the system from another source is the essence of importance sampling,[21] which improves convergence to the state of interest.[22] In the DMC method the propagation of the distribution of walkers is achieved with the short-time approximation, which provides an analytical approximation to the Green's function for small simulation times. In the present study, Ψ_T is written as a product of a HF determinant and a correlation function. The latter

depends explicitly on inter-particle coordinates. The HF calculations were carried out using the GAMESS quantum chemistry package.[23]

The form chosen for the correlation function is the 9-parameter function adapted by Schmidt and Moskowitz[24] from a function introduced by Boys and Handy[25] (SMBH). This function contains two- and three-body terms in the form of electron-electron, electron-nucleus, and electron-other-nucleus distances. The SMBH correlation function contains first-order Jastrow terms[26] that enable the electron-electron and electron-nucleus cusp conditions to be satisfied. Optimization of correlation function parameters is accomplished with fixed sample optimization using the absolute deviation (AD) functional[27] that minimizes the energy of Ψ_T and is given by,

$$AD = \frac{1}{N}\sum_i \left| E_T - E_{L_i} \right| \tag{2}$$

Here N is the number of walkers, E_{L_i} is the local energy of the *ith* configuration, and E_T is reference energy chosen to minimize fluctuations.

A. Transition State and IRC Calculations

The transition state was located at the MP2/6-311++G** level of theory using the Gaussian 98 software package.[28] From the transition state geometry, the reaction path or IRC was calculated. The IRC was determined in both reactant and product directions. The geometry was optimized at each point along the reaction path such that the segment of the reaction path between any two points is described by an arc of a circle and the gradients at the end points of the arc are tangent to the path. The IRC is plotted in Fig. 1.

To provide an assessment of the present DMC computation of atomization energies, heats of reaction and formation, and reaction barrier, we computed these

quantities using the MP2 and B3LYP methods at the complete basis set (CBS) limit. The CBS limit was obtained from an exponential fit to single-point energies for the $cc-pVXZ,\ (X = D, T, \text{and } Q)$ series of basis sets. These calculations were also carried out using the Gaussian 98 program.[28]

III. Results and Discussion

All DMC results were obtained for geometries of the HCl, CH_3OH, and CH_2OH molecules, and transition state optimized at the MP2 level of theory with the 6-311++G** basis set. Results of the geometry optimizations and transition state calculations are given in Tables I and II.

The DMC computations were carried out with 12,800 walkers for a period long enough to obtain stochastic error bars of ≤ 0.3 kcal/mol. There were typically 275-400 blocks and 150-200 moves per block. A small time step of 5×10^{-4} was used to avoid zero time-step extrapolation and to guarantee a high acceptance ratio (99.9%).

A. Transition State and IRC

The optimized TS at the MP2/6-311++G** level of theory indicates that the Cl atom attacks collinearly along a HC methyl bond. The optimized TS geometry is presented in Fig. 2; the geometric parameters are reported in Table II. A vibrational analysis reveals a single imaginary frequency 1056 cm^{-1} with a normal mode along the CH_b bond (see Fig. 2). The zero point energy (ZPE) of 30.26 kcal/mol compares well to previously published value of 30.6 kcal/mol.[12]

The MP2 level of theory yields a barrier to reaction of 2.24 kcal/mol relative to reactant energies; see Table III. This result is 1.24 kcal/mol higher than an earlier MP2/6-311G(d,p) calculation.[12] The computed DMC barrier is 2.39(49) kcal/mol.

The IRC implies that the CH_3OH+Cl reaction occurs in a single step. The IRC confirms the dynamics implied by the CMB[5,6] and REMPI/TOF MS[7] experiments as well as a recent *ab initio* classical dynamics study.[29]

B. Heat of Reaction

An experimental heat of reaction was estimated from literature values of heat of formation of reactants and products.[30-36] The experimental heats of formation of HCl, CH_3OH, and Cl are known to a precision of ±0.1 kcal/mol or less.[35] The heat of formation of CH_2OH is known experimentally to a precision of ~1 kcal/mol; see, refs. 30 and 36. Two experimental heats of reaction at 0K, -7.80(22)[34] and -7.96(31) kcal/mol,[33] have been reported based on different values of the heat of formation of CH_2OH at 0K. At 298 K the heat of reaction is reported to lie in the range of -5.17(98)[36] to -7.36(31) kcal/mol[34] where again the range of values is due to uncertainty of the CH_2OH heat of formation.

The MP2, B3LYP, and DMC heats of reaction are presented in Table IV. The MP2 and B3LYP levels of theory with scaled ZPEs tend to overestimate the heat of reaction by greater than 0.7 kcal/mol at 0K compared to the experimental heats of reaction at 0K. Relative to experiment the MP2 and B3LYP approaches overestimate the heat of reaction at 298 K by more than 0.6 kcal/mol. Using experimental ZPEs, the

calculated heat of reaction at the MP2 and B3LYP levels of theory leads to increased overestimation at 0K and 298K.

The DMC result at 0K with scaled MP2 frequencies was found to be ~1.0 kcal/mol above the experimental value of -7.80(22) kcal/mol.[34] With experimental frequencies the DMC result was in agreement with the experimental value of -7.96(31) kcal/mol.[33] Using experimental ZPEs, the DMC result for the heat of reaction at 298K was found to agree with the experimental heat of reaction of -7.36(31) kcal/mol.[34]

C. Atomization energy

As a test of the DMC computational procedure for the heat of reaction, we calculated the atomization energy and heat of formation of CH_3OH, CH_2OH, and HCl; see Tables V and VI. The atomization energy is defined as the difference of the sum of the energies (valence energies with ECPs) of the atoms and the molecule energy including zero point energy (ZPE) i.e.,

$$E_a^{method} = \sum E^{method}(atoms) - E^{method}(molecule) - E_{ZPE}^{method}(molecule) \quad (3)$$

where "method" corresponds to MP2, B3LYP, and DMC levels of theory.

The ZPEs for the molecules, obtained from B3LYP/6-311++G** and MP2/6-311++G**, calculations, were scaled by 0.9806, and 0.9748, respectively.[37] For the DMC calculations, scaled MP2 frequencies were used. The computed ZPEs obtained for HCl and CH_3OH compare well to experimental values.[38,39]

For CH_2OH, the unscaled ZPEs obtained at the MP2 and B3LYP levels of theory are in good accord with previous theoretical results.[40] However, comparison with experimental ZPE values [33] revealed that the unscaled MP2 and B3LYP frequencies

overestimate the ZPE by 1.5 and 2.2 kcal/mol, respectively. Frequencies scaled by the appropriate scaling factors resulted in ZPE overestimates of 1.1 (MP2) and 1.6 kcal/mol (B3LYP). The use of anharmonic corrections to the calculated frequencies would likely result in closer agreement with experimental frequencies.[33]

The B3LYP (480.64 kcal/mol) and DMC (480.82(40) kcal/mol) atomization energies for CH_3OH are in excellent accord with experiment (480.89 kcal/mol),[35] the MP2 level of theory overestimates the atomization energy by 0.8 kcal/mol. The MP2 and DMC atomization energies for HCl are in excellent agreement with the experimental value of 102.24 kcal/mol.[41] In contrast to CH_3OH, the B3LYP value underestimates experiment by 1.5 kcal/mol.

For CH_2OH, the MP2 and B3LYP levels of theory, including scaled ZPE, overestimate the experimental atomization energy of 386.61(22) kcal/mol[33] by 2.8 and 2.0 kcal/mol, respectively. With the experimental ZPE[33], B3LYP and MP2 levels of theory overestimate the atomization energy by 3.1 and 4.5 kcal/mol, respectively. The DMC result with scaled MP2 frequencies underestimates the atomization energy by 1.6 kcal/mol; with the experimental ZPE, however, the DMC result lies within the experimental range, i.e., between 386.61(22) and 386.45(31) kcal/mol.[33,34]

D. Heat of formation

The heat of formation provides a further estimate of the accuracy of the DMC valence energies. The DMC heats of formation at 0 K and 298K (Table VI) are compared with results from other *ab initio* methods and to experiment. The heat of formation at 298 K was determined by subtracting calculated non-relativistic atomization

energies, E_a, from the standard experimental enthalpies of formation of the isolated atoms. The heats of formation at 0 K and 298 K were obtained from the expressions. [35]

$$\Delta H_f^0(molecule) = \sum \Delta H_f^0(atoms) - E_a \quad (4)$$

$$\Delta H_f^{298}(molecule) = \Delta H_f^0(molecule) - TEMP^{method} \quad (5)$$

where $TEMP^{method}$ is the temperature correction between 0 and 298 K. The latter includes a vibrational contribution computed in the harmonic approximation that has been carried out at the MP2/6-311++G** and B3LYP/6-311++G** levels of theory, a classical description of translation $\left(\frac{3}{2}RT\right)$ and of rotation $\left(\frac{3}{2}RT \text{ for non-linear and } RT \text{ for linear molecules}\right)$, and a temperature correction for the elements C, O, H, and Cl in their standard states extracted from experimental data.[35] The $TEMP^{method}$ calculated for HCl and CH_3OH compares well with $TEMP^{exp}$ defined as,

$$TEMP^{exp} = \Delta H_f^{298K} - \Delta H_f^{0K} \quad (6)$$

The computed TEMP value with MP2 and B3LYP for HCl and CH3OH was 2.07 and 2.70 kcal/mol, respectively.

The heat of formation at 0 K of CH_3OH at the DMC and B3LYP levels of theory are in accord with experiment, while the MP2 results are found to lie 0.8 kcal/mol above the experimental value of -45.4 kcal/mol.[35] The MP2 and DMC results for HCl are within 0.2 kcal/mol of experiment; the B3LYP result lies 1.5 kcal/mol below experiment.[31]

For the heat of formation at 298 K for CH_3OH, the DMC and B3LYP levels of theory agree with the experimental value of -48.00 kcal/mol[35]; MP2 overestimates experiment by 0.8 kcal/mol. For the heat of formation of HCl at 298K, the MP2 and

DMC levels of theory agree with the experimental result of –22.06 kcal/mol, while B3LYP underestimates the heat of formation by 1.5 kcal/mol.

For CH_2OH there are two measured heats of formation at 0K: -2.59(22) [34] and -2.75(31) kcal/mol.[33] Using the scaled ZPE, the MP2 (-5.56 kcal/mol) and B3LYP (-4.73 kcal/mol) results are found to lie above the experimental heat of formation at 0K of –2.75(31) kcal/mol, while the DMC result underestimates the heat of formation at 0K by 1.7 kcal/mol. With the experimental ZPE, MP2 and B3LYP results lie above the largest measured value of the heat of formation by 4.44 and 3.05 kcal/mol, respectively, while the DMC result agrees with this value.[33]

There is a range of experimental results for the heat of formation of CH_2OH at 298K.[30,32-34,36,42] The upper bound of the experimental heat of formation is reported to be -2.15(96) kcal/mol.[36] The lower bound is given as -4.25(31) kcal/mol.[33] The MP2 and B3LYP heats of formation with the scaled calculated ZPEs are >2 kcal/mol below the experimental lower bound, while the DMC value is 0.6 kcal/mol below the experimental upper bound but within experimental uncertainty. Using the experimental ZPE, the MP2 and B3LYP approaches overestimate the heat of formation by >3 kcal/mol. The DMC result of -4.32(41) kcal/mol is in good accord with the experimental lower bound.

Summary and Conclusions

Motivated by recent crossed molecular beam experiment, we have studied theoretically the reaction $Cl + CH_3OH \rightarrow CH_2OH + HCl$. An intrinsic reaction coordinate calculation at the MP2/6-311++G** level of theory was carried out that identified a direct reaction pathway for this reaction that validates the crossed molecular beam findings. The reaction barrier has been computed and found to be 2.24 kcal/mol (MP2) and 2.39(49)

kcal/mol (DMC). The MP2 and B3LYP approaches yield heats of reaction that are larger than the experimental value. The DMC heats of reaction at 0 K and 298 K are found to agree with experiment. Both MP2 and B3LYP methods are found to yield atomization energies and heats of formation in good agreement with experiment except for CH_2OH where significant overestimation is found relative to experiment,. The DMC atomization energies and heats of formation of CH_3OH, HCl, and CH_2OH are found to agree with experiment to within the errors of the two approaches.

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Table I. Optimized structures[a] for CH_3OH, CH_2OH, and HCl.

	Method			
	MP2	B3LYP	MP2	B3LYP
	CH_3OH + Cl		CH_2OH + HCl	
	Distances (Å)			
CH_a	1.0955	1.0969	1.0836	1.0844
CH_b	1.0957	1.0969	-	-
CH_c	1.0894	1.0902	1.0799	1.0796
CO	1.4229	1.4239	1.3679	1.3665
OH_o	0.9600	0.9613	0.9602	0.9231
ClH_b	-	-	1.2737	1.2869
	Angles (degrees)			
H_oOH_a	1.07.20	108.82	108.26	109.93
H_bCO	111.90	112.10	-	-
H_cCH_a	109.76	108.41	120.34	121.73
H_cCO	111.09	112.09	113.73	112.99

[a]All geometry optimizations were carried out using the 6-311++G** basis set; see Fig. 2 for labeling of bond lengths and angles.

Table II. MP2/6-311++G** geometries for the reaction $CH_3OH + Cl$ transition state

Geometry[a]	$Cl\cdots H_b\cdots CH_2OH$
Bond lengths (A)	
CO	1.394
OH_o	0.961
CH_a	1.084
CH_b	1.147
CH_c	1.089
H_bCl	1.796
Angles (degrees)	
COH_o	109.04
OCH_a	108.59
OCH_b	110.91
OH_oCl	114.20
ClH_bC	173.95
Dihedral angle (degrees)	
H_oOCH_a	173.02
H_oOCH_b	-71.36
H_oOCH_c	47.75
ClH_bCO	114.49

[a]See Fig. 2 for labeling of bond lengths and angles.

Table III. Relative energies (including ZPE) with respect to transition state energies at 0 K (kcal/mol).

Method	$Cl \cdots H_b \cdots CH_2OH$(TS) 0K[a]
MP2/6-311++G(d,p)[b]	1.0
MP2[c]	2.24
DMC[d]	2.39(49)

[a]Transition state depicted in Fig. 2; geometric parameters are given in Table II

[b]Reference 12.

[c]This study. MP2 and B3LYP frequencies scaled by 0.98 and 0.97, respectively, see Ref. 37. For DMC results, scaled MP2 frequencies were used. MP2 and B3LYP results are the complete basis set limit values.

[d]Hartree-Fock trial function with 1s core electrons replaced by the SBK ECPs;[14] remaining electrons described with cc-pVTZ basis set.[15]

Table IV. Energies of Cl + CH_3OH relative to CH_2OH + HCl energies at 0 K and 298 K (kcal/mol).

Method	0K			298K		
	w/o ZPE[a]	w/ ZPE_{calc}[b]	w/ $ZPE_{exp.}$[c]	w/o ZPE[a]	w/ $ZPE_{calc.}$[b]	w/ $ZPE_{exp.}$[c]
PMP2[d]	-5.7	-	-	-5.1	-	-
G2[d]	-6.4	-	-	-5.8	-	-
G2MP2[d]	-7.2	-	-	-6.6	-	-
G2/MP2/6-311G(d,p)[e]	-6.19	-	-	-	-	-
MP2[f]	-	-9.80	-10.77	-	-9.27	-10.23
B3LYP[f]	-	-8.72	-9.40	-	-8.07	-8.75
DMC[f,g]	-	-6.99(49)	-7.85(49)	-	-5.82(50)	-7.20(50)
Experiment[h]	-7.80(22)[i],-7.96(31)[j]			-5.17(98)[k] to -7.36(31)[i,l]		

[a]Computed ZPEs of products and reactants not given in Refs. 9,12,29.

[b]Computed ZPEs; for ZPE scaling factors, see footnote c of Table III.

[c]For experimental ZPEs see Refs. 33,39,41.

[d]PMP2 – spin-projected MP2. Results from Ref. 9.

[e]Reference 29; heat of reaction at 298K is not given.

[f]This work; for ZPE scaling factors, see footnote c of Table III.

[g]For DMC trial wave function description, see footnote d of Table III.

[h]Heat for formation of Cl obtained from Ref. 31.

[i]Reference 34.

[j]Reference 33.

[k]Reference 36.

[l]A range of experimental values have been determined for the heat of formation at 298 K for CH_2OH; see Refs. 30,32,34,42.

Table V. Atomization energies (kcal/mol).

Molecule	Methods[a] MP2	B3LYP	DMC[b]	Experiment
CH_3OH	481.70	480.64	480.82(40)	480.89[c,d]
HCl	102.07	100.73	102.31(21)	102.24[c,e]
CH_2OH(scaled zpe)[f]	389.42	388.60	384.94(39)	386.45(31)[h], 386.61(22)[i]
CH_2OH(exp. zpe)[g]	391.06	389.66	386.58(39)	

[a]Atomization energies computed with scaled frequencies unless noted otherwise; see footnote c of Table III for scaling factors.

[b]For DMC trial function description, see footnote d of Table III.

[c]Experimental uncertainty is less than 0.1 kcal/mol. Atomization energy obtained from reference 31

[d]References 31,35; experimental uncertainty is less than 0.1 kcal/mol.

[e]Reference 31.

[f]Determined from scaled computed ZPE.

[g]Determined from experimental ZPE of Ref. 33.

[h]Reference 34.

[i]Reference 33.

Table VI. Heats of formation at 0K and 298 K (kcal/mol).

Molecule	Methods[a] MP2	B3LYP	DMC[b]	Experiment
		0K		
CH_3OH	-46.21	-45.15	-45.33(40)	-45.40[c,d]
HCl	-21.85	-20.51	-22.08(21)	-22.02[c,e]
CH_2OH(scaled zpe)[f]	-5.56	-4.73	-1.08(41)	-2.59(22)[h] , -2.75(31)[i]
CH_2OH(exp. zpe)[g]	-7.19	-5.80	-2.72(40)	
		298K		
CH_3OH	-48.84	-47.79	-47.98(41)	-48.00(10)[d]
HCl	-21.88	-20.54	-22.01(21)	-22.06[c]
CH_2OH(scaled zpe)[f]	-7.24	-6.33	-2.68(40)	-2.15(96)[i] to -4.25(31)[i,k]
CH_2OH(exp. zpe)[g]	-8.80	-7.40	-4.32(41)	

[a]Heats of formation computed with scaled frequencies unless noted otherwise; see footnote c of Table III for scaling factors.

[b]For DMC trial wave function description, see footnote d of Table III.

[c]Uncertainty in experimental values is less than 0.1 kcal/mol. Experimental heat of formation obtained from reference 31

[d]Reference 35.

[e]Reference 31.

[f]Determined from scaled ZPE.

[g]Determined for experimental frequencies; see Ref. 33.

[h]Reference 34.

[i]Reference 33.

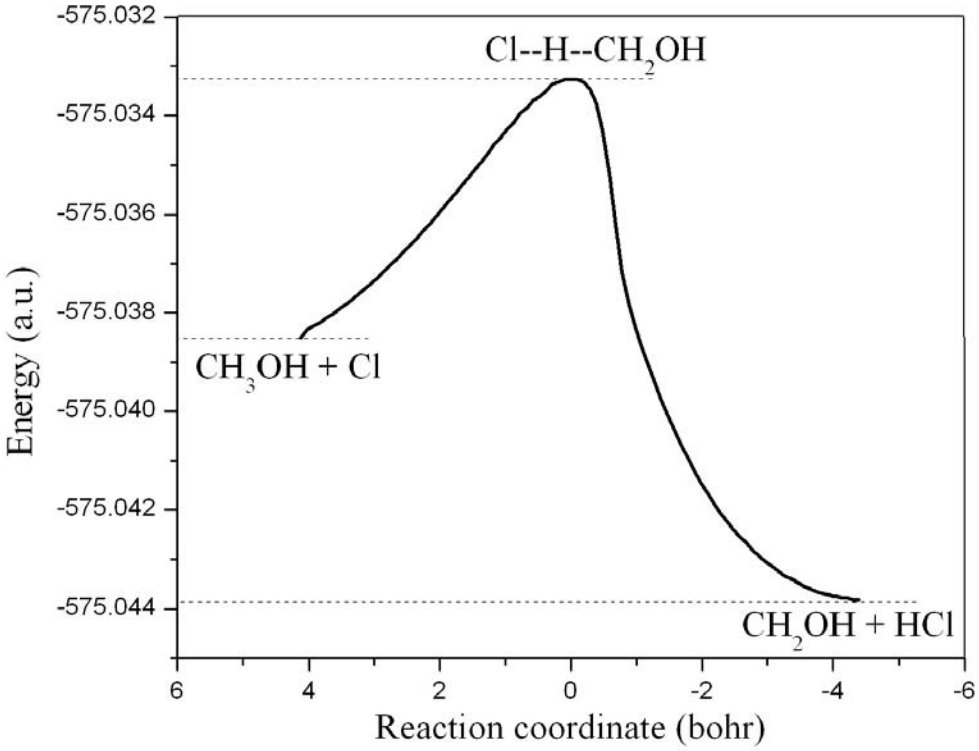
[j]Reference 36.

[k]A range of experimental values have been determined for the heat of formation at 298 K for CH_2OH; see Refs. 30,32,34,42.

Figure Captions

Figure 1. Intrinsic reaction path calculated at the MP2/6-311++G** level of theory. The pathway indicates a direct reaction with no appreciable barrier.

Figure 2. Transition state for the reaction: $CH_3OH + Cl \rightarrow CH_2OH + HCl$. The Cl-atom attacks the methyl hydrogen collinearly; the ClH_bC angle is 173.95° and the ClH_b and H_bC bond lengths are 1.796 and 1.147 Å, respectively. The remaining geometric parameters are presented in the Table II.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-575.034
-575.036
-575.038
-575.040
-575.042
-575.044
Energy (a.u.)
Cl--H--CH2OH
CH3OH + Cl
CH2OH + HCl
6
4
2
0
-2
-4
-6
Reaction coordinate (bohr)

Figure 1

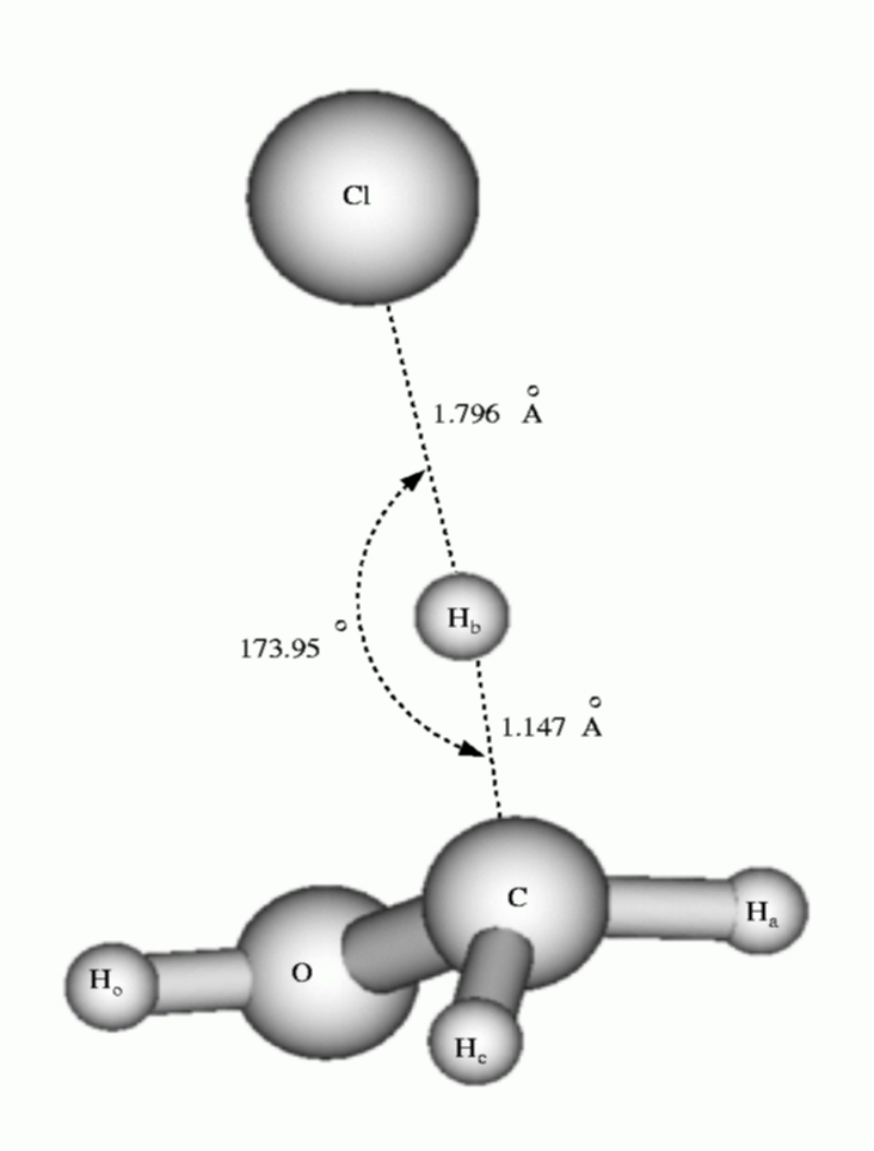

Figure 2