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Kinetics of Hydrogen Abstraction from Chloromethanes by the Hydroxyl Radical: A Computational Study

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Hydrogen abstraction reactions between chloromethanes and the hydroxyl radical have been investigated by using ab initio molecular orbital theory. Geometry optimizations and vibrational frequency calculations have been performed for all the reactants, products, and transition states at the MP2=full/6-311G(d,p) level. Subsequently, single point energy calculations have been carried out at the MP2=full/6-311G(2df,2p) and QCISD(T)/6-311G(2df,2p) levels for all the species. The transition state theory including the tunneling contributions has been used for estimating the rate constants for the hydrogen abstraction. The results obtained from our PMP2 and QCISD(T) calculations with the larger 6-311G(2df,2p) basis set have been found to be in good agreement with the available experimental values.

Introduction

The importance of halocarbons in atmospheric chemistry is well established.[1,2] Chloromethanes are known to be important atmospheric species and should be responsible for the depletion of the ozone layer in the stratosphere and for the greenhouse effects. Partly halogenated alkanes can react with the tropospheric hydroxyl radicals. Since hydrogen abstraction by the hydroxyl radical is the main degradation process of these compounds, the rate of the hydrogen abstraction determines the atmospheric lifetime of such substances. Owing to this importance, a number of experimental works on the kinetics of the hydrogen abstraction from chloromethanes by the hydroxyl radical have been published in the literature.[3−9] There are large differences among the experimentally derived values of the rate constants.[9] For example, in the case of CH_2Cl_2, the rate constants obtained by Hsu and DeMore[9] and by Taylor et al.[8] differ by nearly 38%. Similar differences have been observed in the case of $CHCl_3$ as well.[8]

Several experimental works have been carried out on the hydrogen abstraction reactions between chloromethanes and the hydroxyl radical. Although semiemprical methods were applied for estimating the rate constants of these reactions by using the transition state theory (TST),[10] to the best of our knowledge, no ab initio calculations have been carried out on these reactions. In the present work, we have carried out an ab initio investigation on the following three reactions to calculate the barrier heights and the heats of reaction at various levels of theory.

$$CH_3Cl + {}^{\bullet}OH \rightarrow {}^{\bullet}CH_2Cl + H_2O \tag{R1}$$

$$CH_2Cl_2 + {}^{\bullet}OH \rightarrow {}^{\bullet}CHCl_2 + H_2O \tag{R2}$$

$$CHCl_3 + {}^{\bullet}OH \rightarrow {}^{\bullet}CCl_3 + H_2O \tag{R3}$$

Subsequently, the rate constants have been estimated by using the TST and the values derived from ab initio calculations. Our results described herein are probably the first ab initio results based TST analysis for the hydrogen abstraction from chloromethanes by OH radical.

Computational Methods

The geometries of all the stationary points [the reactants, transition states (TSs), and products] involved in the above-mentioned three reactions were optimized at the second-order Moller−Plesset level of theory, including all the electrons in correlation calculations (MP2=full), using the standard 6-311G(d,p) basis set. Restricted (RMP2) and unrestricted (UMP2) methods were used for the closed- (CH_3Cl, CH_2Cl_2, $CHCl_3$, and H_2O) and open-shell species (${}^{\bullet}CH_2Cl$, ${}^{\bullet}CHCl_2$, ${}^{\bullet}CCl_3$, and ${}^{\bullet}OH$ radicals, as well as the TSs), respectively. Vibrational frequency calculation was carried out to characterize each stationary point. Moreover, to observe the effects of the basis set utilized and of the higher order of electron correlation, single point calculations at the MP2=full/6-311G(2df,2p), and QCISD(T)/6-311G(2df,2p) levels were carried out at the (U)MP2=full/6-311G(d,p) optimized geometries. Thermal corrections to the energies of the stationary points were made by using (U)MP2=full/6-311G(d,p) vibrational frequencies scaled by a factor of 0.9496.[11] The intrinsic reaction coordinate (IRC) calculations were carried out to ascertain that the TSs correspond to the hydrogen abstraction reactions. All the calculations were carried out by using the Gaussian-94 suite of programs.[12]

Results and Discussion

The key geometrical parameters of the three TSs for the reactions R1, R2, and R3 are given in Table 1, whereas those for the reactants and products are given in Table S1 as Supporting Information. Figure 1 displays the structures of the three TSs. The TS structures for the hydrogen abstraction from CH_2Cl_2 (TS_2) and $CHCl_3$ (TS_3) have C_s symmetry with the $C-H_a-O-H_b$ plane bisecting the Cl−C−Cl angle. The TS structure for the hydrogen abstraction from CH_3Cl (TS_1) slightly deviates from C_s symmetry: the $O-H_b$ bond of the OH radical is almost coplanar to the C−Cl bond. We cannot observe a clear

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TABLE 1: Key Geometrical Parameters of the Three Transition States for the Reactions CH_nCl_{4-n} + OH → $CH_{n-1}Cl_{4-n}$ + H_2O (n = 1, 3) (See Figure 1) Optimized at the (U)MP2=full/6-311G(d,p) Level[a]

parameter	(U)MP2	parameter	(U)MP2
CH_3Cl-OH (TS_1)			
$R(C-H_a)$	1.195	$R(O-H_a)$	1.295
$R(O-H_b)$	0.967	$R(H_b...Cl)$[b]	3.14
$\theta(Cl-C-H_a)$	109.3	$\theta(C-H_a-O)$	168.8
$\theta(H_a-O-H_b)$	96.1		
CH_2Cl_2-OH (TS_2)			
$R(C-H_a)$	1.189	$R(O-H_a)$	1.298
$R(O-H_b)$	0.967	$R(H_b...Cl)$[b]	3.35
$\theta(H-C-H_a)$	105.6	$\theta(C-H_a-O)$	171.9
$\theta(H_a-O-H_b)$	96.8		
$CHCl_3-OH$ (TS_3)			
$R(C-H_a)$	1.185	$R(O-H_a)$	1.299
$R(O-H_b)$	0.968	$R(H_b..Cl)$[b]	3.37
$\theta(Cl_1-C-H_a)$	107.0	$\theta(C-H_a-O)$	174.0
$\theta(H_a-O-H_b)$	98.4		

[a] Bond lengths and angles are in Å and degress, respectively. [b] The shortest distance between hydroxyl hydrogen atom (H_b) and a chlorine atom.

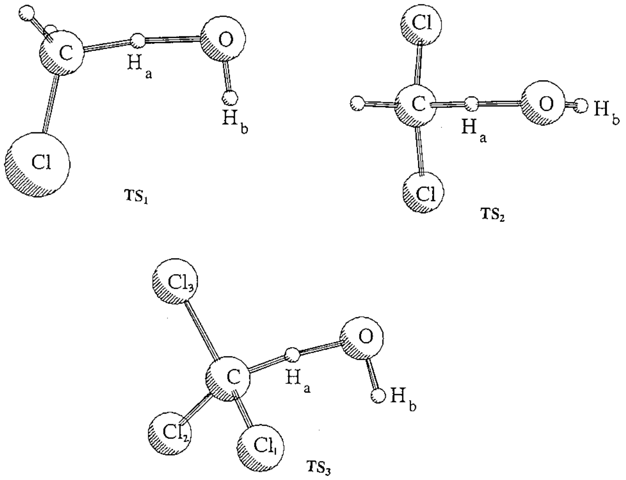

Figure 1. Structures of the three transition states for the hydrogen abstraction reactions of the hydroxyl radical with CH_3Cl (TS_1), CH_2Cl_2 (TS_2), and $CHCl_3$ (TS_3).

TABLE 2: Total Energies (au) and Zero Point Vibrational Energies (ZPVE in kcal/mol) of All the Stationary Points Involved in Reactions R1, R2, and R3 (PMP2 Results in Parentheses)

molecule	MP2[a]	MP2[b]	QCISD(T)[b]	ZPVE[c]
CH_3Cl	−499.494112	−499.584646	−499.547013	24.2
CH_2Cl_2	−958.590792	−958.745439	−958.662678	19.0
$CHCl_3$	−1417.684450	−1417.904207	−1417.775023	13.0
$^{\bullet}CH_2Cl$	−498.828773 (−498.831129)	−498.916380 (−498.919002)	−498.878814	14.7
$^{\bullet}CHCl_2$	−957.930561 (−957.932902)	−958.082609 (−958.085307)	−958.000458	10.3
$^{\bullet}CCl_3$	−1417.028062 (−1417.030441)	−1417.245691 (−1417.248469)	−1417.117567	4.8
CH_3Cl-OH (TS_1)	−575.071096 (−575.076026)	−575.201098 (−575.206325)	−575.164513	28.0
CH_2Cl_2-OH (TS_2)	−1034.169369 (−1034.174027)	−1034.363402 (−1034.368375)	−1034.282145	22.5
$CHCl_3-OH$ (TS_3)	−1493.264687 (−1493.269101)	−1493.523926 (−1493.528666)	−1493.396208	16.3
$^{\bullet}OH$	−75.591398 (−75.592894)	−75.628625 (−75.630408)	−75.627126	5.5
H_2O	−76.282896	−76.326500	−76.319499	13.7

[a] 6-311G(d,p) basis set. [b] 6-311G(2df,2p) basis set. [c] MP2=full/6-311G(d,p)

TABLE 3: Harmonic Vibrational Frequencies of the Stationary Points for the Hydrogen Abstraction by Hydroxyl Radical from the Chloromethanes (Frequencies Calculated at the (U)MP2=full/6-311G(d,p) Level of Theory)

system	frequencies (cm^{-1})
CH_3Cl	787, 1065, 1065, 1442, 1496, 1496, 3125, 3233, 3233
CH_2Cl_2	303, 752, 818, 926, 1233, 1361, 1478, 3173, 3248
$CHCl_3$	280, 280, 385, 697, 820, 820, 1292, 1292, 3226
$^{\bullet}CH_2Cl$	250, 880, 1047, 1473, 3243, 3397
$^{\bullet}CHCl_2$	323, 547, 793, 938, 1316, 3288
$^{\bullet}CCl_3$	293, 293, 367, 521, 939, 939
$^{\bullet}OH$	3861
H_2O	1667, 3910, 4017
CH_3Cl-OH (TS_1)	2011i, 60, 141, 290, 753, 780, 860, 1051, 1132, 1295, 1469, 1478, 3162, 3260, 3846
CH_2Cl_2-OH (TS_2)	2042i, 36, 130, 150, 308, 695, 753, 843, 849, 1040, 1136, 1318, 1454, 3203, 3839
$CHCl_3-OH$ (TS_3)	2036i, 42, 95, 117, 283, 284, 340, 508, 739, 843, 865, 892, 1163, 1408, 3839

hydrogen bonding interaction between the hydroxyl hydrogen and a chlorine atom in the TSs. The shortest H_b...Cl distances in the three TSs are found to be longer (3.14−3.37 Å) than the sum of van der Waals radii of the hydrogen and chlorine atoms (3.0 Å).[13] However, in the TS structures of CH_3Cl (TS_1) and CH_2Cl_2 (TS_2), the hydroxyl hydrogen is located closer to a chlorine atom than to the hydrogen atom in the CX_3 moiety (CX_3...H...OH). Electrostatic interactions between these two atoms should not be very pronounced but should be responsible for the overall TS structures. The $C-H_a-O$ angles increase in the order $CH_3Cl < CH_2Cl_2 < CHCl_3$. The breaking C−H bond length (1.185−1.195 Å) and the forming O−H bond length (1.295−1.299 Å) do not vary significantly in the three TSs. The total energies and the harmonic vibrational frequencies for the stationary points are presented in Tables 2 and 3, respectively. Because of spin contamination, the spin-projected MP2 (PMP2) energies for the TSs are significantly lower than the corresponding MP2 energies.

The barrier heights ($\Delta E_0^{\ddagger} = E_{TS} - E_A - E_B$, where E's are the total energies of the TS and the reactants including the zero point vibrational energies) and the heats of reaction [ΔH(298 K)] obtained at the various levels of theory are presented in Table 4. It is well-known that the reaction barriers may be overestimated by up to 10 kcal/mol at the MP2 level due to serious spin contamination.[14] The barrier heights obtained from the PMP2 energies are thus considered to be more reliable.[15] In the present cases, the reaction barriers obtained from the MP2 energies are found to be more than 2 kcal/mol higher than those obtained from the corresponding PMP2 energies. The effect of basis set on the reaction barriers can be observed from our MP2 results with two different basis sets, namely 6-311G(d,p) and 6-311G(2df,2p). The barrier heights decrease by nearly 1.5 kcal/mol with the increase in basis set at the MP2 level. The QCISD(T) barrier heights are found to be close to those obtained from the PMP2 calculations with the larger basis set. It seems that the PMP2 calculations with the larger basis set can provide a better alternative than computationally expensive QCISD(T) calculations. Similar observations were made earlier from the results on difluoroethanes.[16]

The procedure of searching for the energy maximum along the IRC (IRCMAX) proposed by Petersson and co-workers[17,18] can be used to ascertain the position of the TS at a higher level of theory [such as QCISD(T)/6-311G(2df,2p)] from an IRC path calculated at a lower level [such as UMP2/6-311G(d,p)]. The method requires single point energy calculations at the higher level of theory for some selected points along the lower level IRC path. Since geometry optimization at the sophisticated level

TABLE 4: Classical Barrier Heights ($\Delta E_0^{\ddagger}$ in kcal/mol) and Heats of Reaction [ΔH(298 K) in kcal/mol] Obtained at the Various Levels of Theory for the Hydrogen Abstraction Reactions between Chloromethanes and the Hydroxyl Radical (Corresponding PMP2 Results in Parentheses)

	$\Delta E_0^{\ddagger}$			$-\Delta H$(298 K)			
reaction	MP2[a]	MP2[b]	QCISD[c]	MP2[a]	MP2[b]	QCISD[c]	expt[d]
$CH_3Cl + OH$ (R1)	7.38 (5.23)	5.97 (3.81)	4.38	17.1 (17.6)	19.2 (19.8)	15.9	18.3
$CH_2Cl_2 + OH$ (R2)	6.15 (4.16)	4.79 (2.79)	2.91	19.8 (20.3)	22.1 (22.7)	19.1	20.2
$CHCl_3 + OH$ (R3)	4.92 (3.09)	3.50 (1.66)	1.65	21.7 (22.3)	24.4 (25.0)	21.6	23.4

[a] MP2=full/6-311G(d,p) level. [b] MP2=full/6-311G(2df,2p)//MP2=full/6-311G(d,p) level. [c] QCISD(T)/6-311G(2df,2p)//MP2=full/6-311G(d,p) level. [d] Reference 20.

of theory, such as QCISD(T), is still computationally prohibitive except for very small molecules, the IRCMAX method can be very useful for determining the TS structure and barrier height at a higher level of theory from a lower level IRC path. We calculated the energies at the UMP2/6-311G(2df,2p) level for the CH_3Cl-OH, CH_2Cl_2-OH, and $CHCl_3-OH$ systems at the five points around each TS (two points on each side of the TS) along the IRC path calculated at the UMP2/6-311G(d,p) level with a step size of 0.1 au. The positions of the three TSs were found to be the same when one goes from the lower level to the IRCMAX calculations at the higher level. Thus, the barrier heights obtained from the UMP2/6-311G(2df,2p)//UMP2/6-311G(d,p) and Max{UMP2/6-311G(2df,2p)}//IRC{ UMP2/6-311G(d,p)} were found to be the same. The IRCMAX calculations were also carried out at the QCISD(T)/6-311G(2df,2p) level for the CH_3Cl-OH system. Once again, the barrier height obtained from the IRCMAX calculations was found to be the same as obtained from the single point calculation at the TS. Similar results were seen for the hydrogen abstraction reactions between CH_4 and OH, where QCISD/6-311G(d,p)//MP2/6-31G-(d) and IRC(QCISD/6-311G(d,p)//IRC{MP2/6-31G(d)}) barrier heights were found to be almost the same.[17] Due to huge computational cost, the IRCMAX calculations at the QCISD-(T) level for the CH_2Cl_2-OH and $CHCl_3-OH$ systems were not performed. However, from the results at the UMP2/6-311G-(2df,2p) level, it can be expected that the IRCMAX barrier heights for the CH_2Cl_2-OH and $CHCl_3-OH$ systems will not be significantly different from those obtained from our single point calculations. It should be pointed out that although the barrier heights obtained from the single point calculations and the IRCMAX calculations are the same, the barrier width may change at the higher level of theory. We observed from the IRCMAX calculations that the shape of the reaction barriers obtained from the UMP2/6-311G(d,p) and the UMP2/6-311G-(2df,2p) methods remain almost unchanged. However, it was observed from the QCISD(T) results for only the CH_3Cl-OH system that the shape of the barrier does change when one goes from the UMP2/6-311G(d,p) to QCISD(T)/6-311G(2df,2p) level of theory. The change in barrier width at the QCISD(T) level will certainly have some influence on the reaction rate constant at lower temperature because tunneling correction to the reaction rate depends on the barrier width. Since the IRCMAX calculations at the QCISD(T) level could be performed only for the CH_3Cl-OH system and the rate constants obtained from the QCISD(T) results are given only as Supporting Information (discussed later), the effect of change in barrier width on the reactions rate constants is not determined explicitly in the present work.

The heats of reaction [ΔH(298 K)] presented in Table 4 show that the three reactions (R1, R2, and R3) are exothermic in nature. The exothermicity increases with the increase in chlorine substitution from CH_3Cl to $CHCl_3$ through CH_2Cl_2. The reaction barriers decrease in the same order. This observation is in accord with the suggestion of Evans and Polanyi.[19] They pointed out that barrier heights for the atom transfer reactions should decrease with the increase in exothermicity.[19] The values for heats of reaction calculated at the MP2 levels are in reasonably good agreement with the values estimated from the experimental thermochemical data.[20] Spin contamination in the chloromethyl and hydroxyl radicals is much less compared to that observed in the TSs: the values of $\langle S^2 \rangle$ for chloromethyl radicals and hydroxyl radical do not exceed 0.766, while the values of $\langle S^2 \rangle$ for the TSs are around 0.778. Thus, the differences between the MP2 and PMP2 values for the heats of reaction are much less significant than those for the barrier heights. The values of heats of reaction obtained from the QCISD(T) calculations are found to underestimate the exothermicities of the three reactions. Similar observations were made earlier in the case of difluoroethanes[16] and dichloroethanes.[21] Thus, probably MP2 calculations with a larger basis set can be more useful than the higher order calculations, such as QCISD(T), with a smaller basis set.

Rate Constants

The rate constants for the hydrogen abstraction from chloromethanes were calculated by using the standard TST expression:[22]

$$k_{\mathrm{TST}} = \Gamma \frac{k_{\mathrm{B}}T}{h} \frac{Q_{\mathrm{TS}}}{Q_{\mathrm{A}}Q_{\mathrm{B}}} e^{-\Delta E_0^{\ddagger}/RT}$$

where Γ is the transmission coefficient, Q's are the respective partition functions and $\Delta E_0^{\ddagger}$ is the barrier height calculated from the energy difference (including the zero point vibrational energy) between the TS and the reactants. The value of Γ was calculated by using Wigner's empirical formula[23] and also by following the procedure of Eckart's unsymmetric barrier method.[24] In Wigner's empirical formula, the transmission coefficient for tunneling is calculated using the expression: $\Gamma(T) = 1 + (h\nu^*/k_{\mathrm{B}}T)^2/24$, where ν^* is the imaginary frequency associated with the TS. In Eckart's method, the transmission coefficient is calculated as an integrated sum of the energy dependent transmission probability. Garrett and Truhlar[25] observed in several simple reactions that Wigner's transmission coefficient gives good overall agreement with more elaborate calculations. The vibrational partition functions were evaluated with the quantum harmonic approximation using the frequencies (scaled by a factor of 0.9496) calculated at the (U)MP2/6-311G-(d,p) level. The electronic partition function of the OH radical was evaluated by taking into account the splitting of 139.7 cm^{-1} in the $^2\Pi$ ground state.[26] Since the vibrational frequencies associated with the rotational motion of the OH radical in the three TSs were found to be very low (60, 36, and 42 cm^{-1} for the TS_1, TS_2, and TS_3, respectively; see Table 3), these modes were treated as a free rotator around the H_a...O axis. The barrier heights obtained from PMP2 and QCISD(T) calculations with the 6-311G(2df,2p) basis set were used for the TST calculations. However, since the difference between barrier heights obtained

TABLE 5: Calculated Rate Constants and Comparison with Other Works

reactant	k(298 K)[a]	A factor[a]	E/R	G	ref
CH_3Cl	4.5×10^{-14}	1.8×10^{-11}	1841	4.9	this work[b]
	1.3×10^{-13}	1.0×10^{-11}	1409	14.2	this work[c]
	3.5×10^{-14}	1.1×10^{-11}	1712		Taylor et al.[8]
	3.1×10^{-14}	4.4×10^{-12}	1470		Hsu and DeMore[9]
	3.6×10^{-14}	4.0×10^{-12}	1400		JPL-97[25]
	4.4×10^{-14}				Perry et al.[4]
CH_2Cl_2	9.0×10^{-14}	8.2×10^{-12}	1399	5.1	this work[b]
	1.0×10^{-13}	5.7×10^{-12}	1171	8.6	this work[c]
	1.5×10^{-13}	6.0×10^{-12}	1096		Taylor et al.[8]
	9.2×10^{-14}	3.2×10^{-12}	1057		Hsu and DeMore[9]
	1.1×10^{-13}	3.8×10^{-12}	1050		JPL-97[25]
	1.4×10^{-13}				Perry et al.[4]
$CHCl_3$	2.1×10^{-13}	3.9×10^{-12}	927	5.0	this work[b]
	1.7×10^{-13}	3.5×10^{-12}	982	4.0	this work[c]
	1.1×10^{-13}	1.2×10^{-12}	714		Taylor et al.[8]
	8.8×10^{-14}	1.2×10^{-12}	780		Hsu and DeMore[9]
	1.0×10^{-13}	2.0×10^{-12}	900		JPL-97[25]

[a] In units of cm^3 molecule^{-1} s^{-1}. [b] TST with the barrier height obtained at the PMP2=full/6-311G(2df,2p) level and Wigner's tunneling correction. [c] TST with the barrier height obtained at the PMP2=full/6-311G(2df,2p) level and Eckart's tunneling correction.

from these two levels of theory is found to be insignificant for CH_2Cl_2 and $CHCl_3$ and less than 0.6 kcal/mol for CH_3Cl, the results obtained from the PMP2 barrier heights are discussed here. The results obtained from the QCISD(T) barrier heights are given as Supporting Information (Figure S1).

The TST calculations were performed to estimate the rate constants in the temperature range from 295 to 895 K. The Arrhenius parameters were evaluated in this temperature range by fitting log k against 1/*T*. Table 5 presents the rate constants at 298 K and the Arrhenius parameters derived from the TST calculations along with the corresponding experimental values. The TST calculated rate constants are found to be in reasonable agreement with the experimental values. The *A* factors derived from the least-squares fittings are found to be in almost the same order as the experimental values. The values of activation energies (*E*/*R*) obtained from the fittings deviate less than 1 kcal/mol from the experimental values. In addition, the transmission coefficients obtained from Wigner's and Eckart's tunneling corrections are not much different. However, Eckart's correction gives the value of transmission coefficient about 3-fold larger at 298 K than Wigner's correction for the reaction R1 (14.2 vs 4.9).

Taylor et al.[8] reported the rate constants in a wide range of temperature for hydrogen abstraction from chloromethanes, and thus, their results can be compared with the rate constants derived from our TST calculations. Parts A–C of Figure 2 show the Arrhenius plots of the TST calculated and experimental[8] rate constants for the hydrogen abstraction from CH_3Cl, CH_2Cl_2, and $CHCl_3$, respectively. For the hydrogen abstraction from CH_3Cl, the TST calculated rate constants with Wigner's tunneling correction are in quite good agreement with the experimental values over a wide temperature range. Eckart's correction tends to give rate constants slightly larger than the experimental values in the lower temperature range. For the hydrogen abstraction from CH_2Cl_2, the TST calculated rate constants are slightly smaller than the experimental values. Conversely, for the hydrogen abstraction from $CHCl_3$, the TST calculated values are slightly larger compared to the experimental values. However, all the results considered, the TST calculated rate constants are in reasonable agreement with the experimental values. The deviation of the TST calculated values from the experimental values is usually found to be less than 0.5 in log *k* unit. The largest deviation is around one in log *k* unit for the reaction R1: Eckart's correction gives the value of the rate constant about 1 order larger than the experimental value in the lower temperature range.

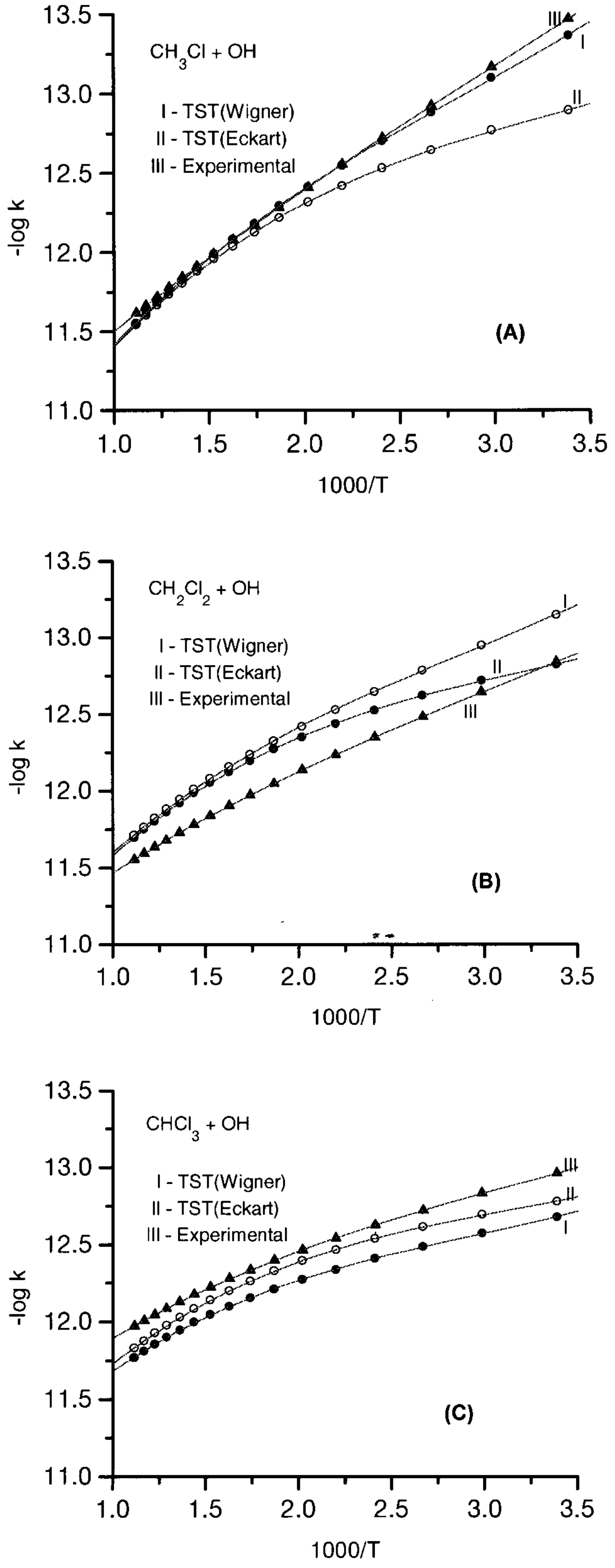

Figure 2. Arrhenius plot of the rate constants for the hydrogen abstraction reactions of OH radical with CH_3Cl (A), CH_2Cl_2 (B), and $CHCl_3$ (C) calculated by the transition state theory and using the barrier heights obtained at the PMP2=full/6-311G(2df,2p) level of theory. The points marked by solid squares indicate the experimental values (ref 8).

Summary and Conclusions

The stationary points along the reaction coordinates for the hydrogen abstraction by OH radical from chloromethanes were located at the (U)MP2/6-311G(d,p) level. Subsequently, the barrier heights were calculated from the single point calculations at different levels of theory, such as (U)MP2/6-311G(2df,2p) and QCISD(T)/6-311G(2df,2p). The rate constants for the hydrogen abstractions were estimated by using the standard TST. The rate constants obtained from the (U)MP2/6-311G(2df,2p) barrier heights are found to be in reasonable agreement with the corresponding experimental values. The heats of reaction are also well estimated at the same level of theory. Experimental results showed that the barrier height for the hydrogen abstraction from chloromethanes decreases on the order of CH_3Cl > CH_2Cl_2 > $CHCl_3$,[8,9,27] whereas the exothermicity of the reactions decreases in the opposite order.[20] These observations are in accord with the suggestions of Evans and Polanyi[19] and our calculations reproduced well these observations.

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Supporting Information Available: Table S1 of key geometrical parameters of the reactants and products and Figure S1 of an Arrhenius plot of the rate constants obtained from the QCISD(T) barrier heights. This material is available free of charge via the Internet at http://pubs.acs.org.

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