

Ab initio direct dynamics studies on the reactions of chlorine atom with $\text{CH}_3 - \text{Cl}_n\text{CHO}$ ($n = 1-3$)

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Abstract

The H-abstraction reactions $\text{CH}_3 - \text{Cl}_n\text{CHO} + \text{Cl}$ ($n = 1-3$) ((R1)–(R3)) have been studied by the ab initio direct dynamics method. The potential energy surface (PES) information required for the rate constant calculation for each reaction is obtained at the MP2/cc-pVDZ and CCSD(T)/6-311+G(d,p) (single-point) levels of theory. The hydrogen atom can be abstracted from both the formyl (–CHO) positions and the chlorinated methyl (– $\text{CH}_3 - \text{Cl}_n$) positions for CH_2ClCHO , CHCl_2CHO , i.e., there are two probable channels for reactions (R1) and (R2). The enthalpies of formation for the species CH_2ClCHO , CHCl_2CHO , CCl_3CHO , and the radicals CH_2ClCO , CHClCHO , CHCl_2CO , CCl_2CHO , CCl_3CO are computed at the CCSD(T)/6-311+G(d,p)//MP2/cc-pVDZ level. The rate constants for each reaction channel are evaluated by using improved canonical variational transition state theory (ICVT) with a small-curvature tunneling correction (SCT) over a wide range of temperatures from 220 to 2000 K. The calculated ICVT/SCT rate constants are found to be in good agreement with the available experimental values. It is shown that in the low temperature range, the reactions proceed predominantly via H-abstraction from formyl position, while the other H-abstraction channel from methyl should be taken into account with the increase of the temperature. Also, the reactivity decreases substantially with chloride substitution at the methyl position of acetaldehyde.

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1. Introduction

Chlorofluorocarbons (CFCs) are being phased out because of their well-known connection with stratospheric ozone destruction and greenhouse effects. Hydrofluorocarbons (HFCs) and hydrochlorofluorocarbons (HCFCs), which are considered to be an important classes of potential CFCs substitutes used in a number of industrial applications, attracted considerable attention [1–3]. Halogenated aldehydes can be produced as the main oxidation product of several HFCs and

HCFCs, and they are also regarded as important reaction intermediates in the atmosphere [3–5]. Furthermore, these degradation products containing halogens produced may still transport halogen to the stratosphere and destruct the ozone layer. It is, thus, necessary to perform the kinetic investigation for these halogenated aldehydes in order to determine their atmospheric lifetime. In the present study, the focus is on the degradation of the chlorinated aldehydes $\text{CH}_3 - \text{Cl}_n\text{CHO}$ ($n = 1-3$) initiated by Cl atoms, which is a convenient substitute in laboratory experiments for the attack by OH radicals since halogens are more easily generated than OH radicals. The rate constants for the reaction $\text{Cl} + \text{CH}_3 - \text{Cl}_n\text{CHO}$ ($n = 1-3$) have been determined at room temperature [6–9], while it is found that there

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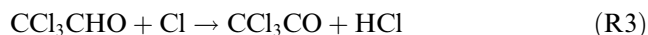
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are lack of the other kinetic data, such as the temperature dependence of the rate constants over a wide temperature range, the activation energies and the reaction enthalpies. So the aim of this paper is to perform the theoretical investigations for the title reactions in order to provide further information concerning them.

For the chlorine-substituted acetaldehydes, the hydrogen atom can be abstracted from formyl ($-\text{CHO}$) positions and methyl ($-\text{CH}_3$ – Cl_n) positions; as a result, two reaction pathways are feasible for CH_2ClCHO and CHCl_2CHO with Cl atoms, i.e.



And one pathway is available for CCl_3CHO with Cl atom, i.e.



Here, a dual-level (X//Y) direct dynamics method [10–12] is applied to study the above reaction. As usual, X//Y refers to optimization and frequencies at lower-level Y with single-point energies calculated at higher-level X. In this approach, the potential energy surface (PES) information obtained directly from ab initio electronic structure calculations is input into the Polyrate 8.4.1 [13] to perform the variational transition state theory (VTST) [14–16] calculations. The comparison between theoretical and experimental results is discussed.

In addition, it is known that the knowledge of the enthalpy of formation of the species is important in the thermodynamic properties as well as in the kinetics of atmospheric processes. However, most of the species involved in the three reactions have been little studied experimentally. In the present study, the enthalpies of formation for the reactants and products radicals are estimated theoretically by using the isodesmic reactions [17].

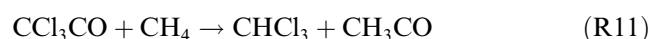
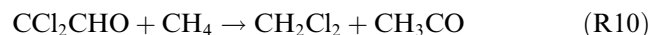
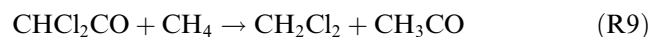
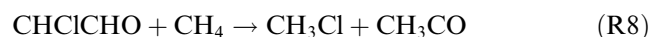
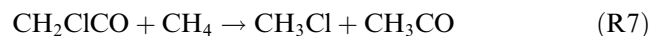
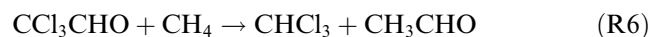
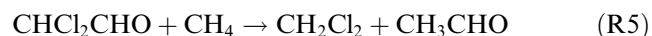
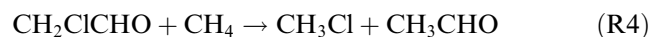
2. Calculation methods

The electronic structure calculations are carried out by the Gaussian 03 program [18]. The geometries and frequencies of all the stationary points including reactants, transition states (TSs), products, and complexes are optimized by using restricted or unrestricted second-order Møller-Plesset perturbation theory with the correlation-consistent polarized double-zeta basis sets of Dunning and co-worker [19], denoted as MP2/cc-pVDZ. Due to the lack of the available experimental data for the reactants and products except for HCl, the optimization calculations for them are also done

using modified Perdew-Wang 1-parameter-method for kinetics method with 6-31+G(d,p) basis set (MPW1K/6-31+G(d,p)) [20] to testify the accuracy of the structures at the MP2/cc-pVDZ level. At the MP2 level, the minimum energy path (MEP) is obtained by the intrinsic reaction coordinate (IRC) theory to confirm that the TS really connects to minimum along the reaction path. In order to obtain more reliable energetics, single-point energy calculations for the stationary points and a few extra points along with the MEP are carried out at the coupled-cluster approach with single and double substitutions including a perturbative estimate of connected triples substitutions (CCSD(T)) level with the basis set 6-311+G(d,p) using the MP2 geometries. The energy profiles are further refined with interpolated single-point energies (ISPE) method [21].

By means of the POLYRATE-Version 8.4.1 program [13], the theoretical rate constant for each reaction channel is calculated using the conventional transition state theory (TST) and the improved canonical variational transition state theory (ICVT) with the small-curvature tunneling correction (SCT) approximation proposed by Truhlar and co-workers [22,23]. During the kinetic calculations, the Euler single-step integrator with a step size of $0.001 \text{ (amu)}^{1/2}$ is used to follow the MEP, and the generalized normal-mode analysis is performed every $0.01 \text{ (amu)}^{1/2} \text{ bohr}$. Vibrations are treated by rectilinear method at nonstationary points. The $^2\text{P}_{3/2}$ and $^2\text{P}_{1/2}$ electronic states of the Cl atom, with an 881 cm^{-1} splitting due to spin-orbit coupling, are used in the calculation of the electronic partition functions. The curvature components are calculated using a quadratic fit to obtain the derivative of the gradient with respect to the reaction coordinate. The total rate constant is obtained from the sum of the individual rate constant.

In addition, in order to give theoretical prediction for the enthalpies of formation ($\Delta H_{f,298}^0$) of the species which have been little studied experimentally, we perform the calculations at the MP2/cc-pVDZ and CCSD(T)/6-311+G(d,p) (single-point energy) levels by using the following isodesmic reactions:



3. Results and discussion

3.1. Stationary points

The optimized structures of all the stationary points (including the reactants, product radicals, complexes, and transition-states) at the MP2/cc-pVDZ level are displayed in Fig. 1. For comparison, density functional theory (DFT) calculations are done by MPW1K method using the 6-31+G(d, p) basis set. It is seen that the geometries for the reactants and products radicals optimized at the two levels are in good mutual agreement with each other. The molecules CHCl_2CHO and CCl_3CHO have C_s symmetry, with H4-C1-C2-O3 dihedral angle equal to 180.0° , while no symmetry is found with respect to CH_2ClCHO molecule, with the dihedral angle Cl5-C1-C2-O3 of 142.8° and 147.5° at the MP2 and MPW1K level, respectively. The C–O bond distance decreases and the C–C bond distance increases substantially with halogen substitution at the methyl position of acetaldehydes. Apparently, the high electron negativ-

ity of the chlorine atom is responsible for the changes of the bond distance. All of the product radicals possess C_s symmetry. In comparison with RCO radicals and the corresponding parent chloroacetaldehydes, the C–C bond distance in RCO radicals becomes longer and C–O bond distance becomes shorter, while for products CHClCHO and CCl_2CHO both the C–C and C–O bond lengths become shorter. In the three transition states TS1a–3a, the reactive C–H bond which is broken is elongated by 4.5%, 6.4%, and 7.3% as compared to the C–H equilibrium bonds length of the corresponding Cl-substituted acetaldehydes and the forming bond H–Cl is longer than the equilibrium bond length of HCl by 44.5%, 36.8%, and 34.1%, respectively. The elongation of the breaking bond (C–H) is much less than the elongation of the forming bond (H–Cl), indicating that the transition states are reactant-like, so the three reactions may proceed via “early” transition states, and it is seen that TS1a should be the earliest among the three TSs. In the case of TS1b and TS2b, similar observation is made at the MP2 levels. The breaking C–H bonds are

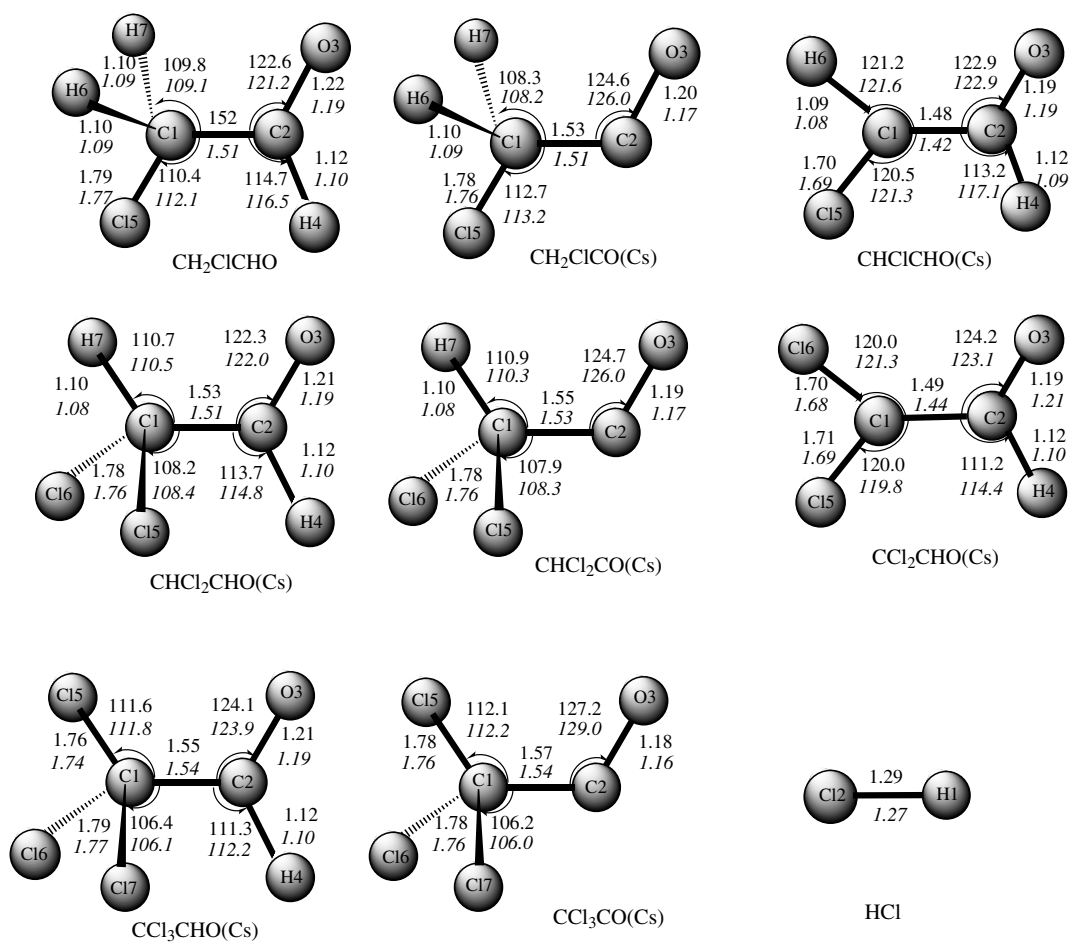


Fig. 1. Optimized geometries parameters (in Å and degree) of the reactants, products, transition states (TSs), and hydrogen-bond complexes at the MP2/cc-pVDZ and MPW1K/6-31+G(d, p) levels. The italic values are obtained at the MPW1K/6-31+G(d, p) levels.

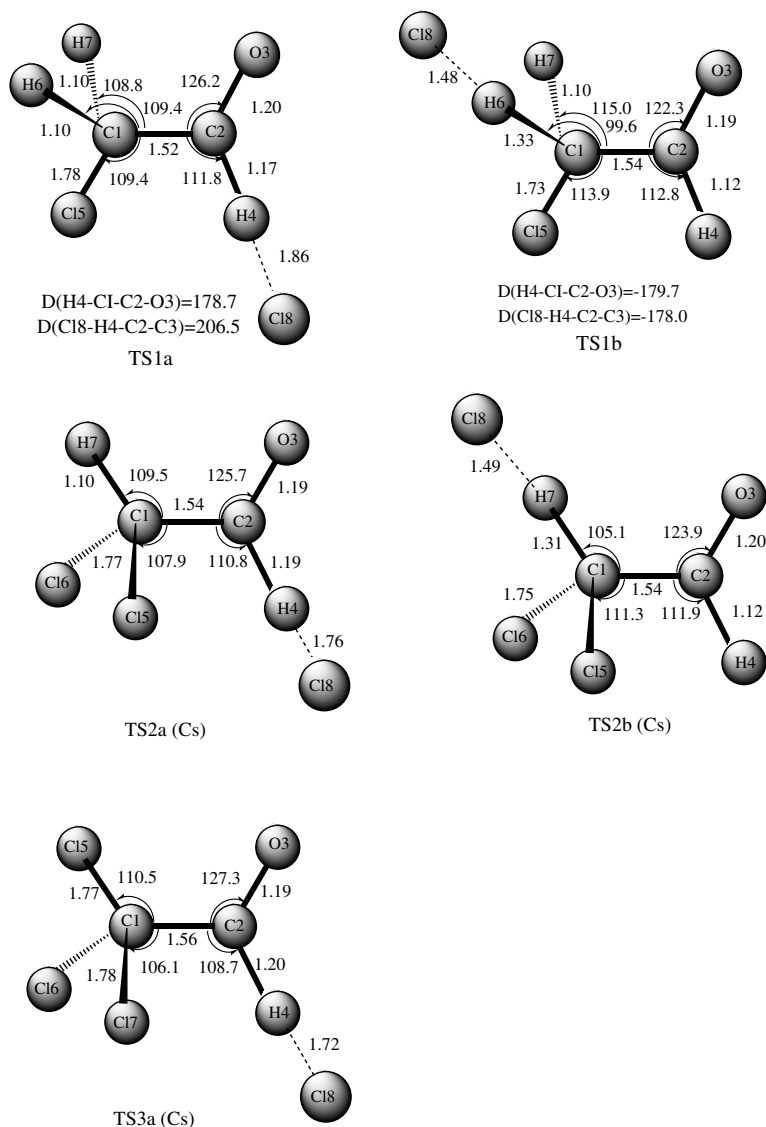


Fig. 1 (continued)

increased by 20.6% and 19.4% and the forming H–Cl bonds are stretched by 15.0% and 15.8%, respectively, with respect to the regular bond length.

In addition, three hydrogen-bonded complexes with energies less than the products are located at the exit channels of reactions (R1a), (R2a) and (R3), respectively, which means that the reactions may proceed via an indirect mechanism. In the complexes structures, the O···H' bond distances are 3.15, 3.20, and 3.20 Å, respectively, and the other bond lengths are very close to those of the products.

The harmonic vibrational frequencies of all the stationary points calculated at the MP2/cc-pVDZ and MPW1K/6-31+G(d,p) levels are listed in Table 1, as well as the available experimental value for HCl [24]. It is found that the MP2 frequencies are in good agreement with the corresponding MPW1K values. The reactants, products and complexes correspond to all real

frequencies, and the transition states are confirmed to have only one imaginary frequency. The normal mode associated with the imaginary frequency of the TS corresponds to the coupling of the breaking and the forming bonds stretching vibrational modes. Also, it is seen that there are quite different imaginary frequencies for the H-abstraction reaction channels from formyl position and halogenated-methyl position. For example, the imaginary frequencies are 411i for (R1a) and 1284i for (R1b).

Due to the lack of the reliable experimental enthalpies of formation ($\Delta H_{f,298}^0$) for the great majority of the species included in the reactions, here, we estimate the $\Delta H_{f,298}^0$ values of all the reactants and products using isodesmic reactions (R4)–(R11). Since the isodesmic reaction is using the conservation of the number of electron pairs in the reactions and products the changes in their correlation energies are usually small, it is known

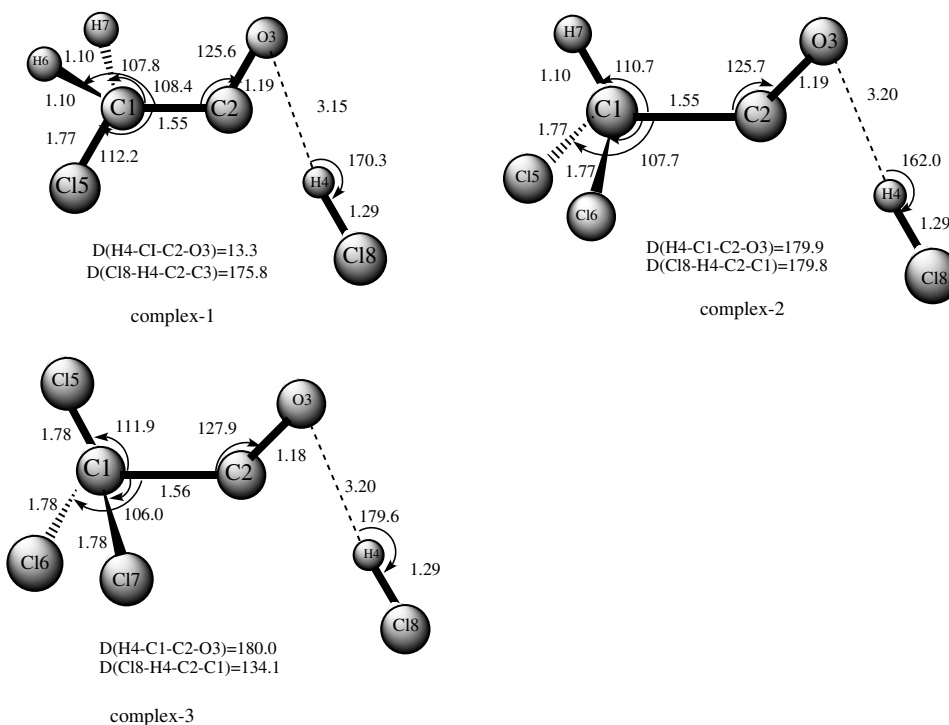


Fig. 1 (continued)

to provide quite accurate reaction energies. In the calculation, the known heats of formation of the reference compounds [25] (CH_4 , -17.83 kcal/mol; CHCl_3 , -24.57 kcal/mol; CH_2Cl_2 , -22.74 kcal/mol; CH_3Cl , -19.92 kcal/mol; CH_3CHO , -40.64 ± 0.36 kcal/mol; CH_3CO , -2.86 ± 0.71 kcal/mol) are involved. The calculated $\Delta H_{f,298}^0$ values at the CCSD(T)/6-311+G(d,p)//MP2/cc-pVDZ level are given in Table 2, along with the available experimental values [26,27]. Seen from the table, good agreement between theory and experiment is obtained when the experimental uncertainty is considered. As a result, it might be inferred that the same accuracy is expected for the $\Delta H_{f,298}^0$ values of the other species whose data are unknown.

The reaction enthalpies (ΔH_{298}^0) for the three reactions at the MP2/cc-pVDZ and CCSD(T)/6-311+G(d,p)//MP2 levels along with the experimental data are listed in Table 3. Also, a schematic potential energy surface of each reaction with zero-point energy (ZPE) corrections is plotted in Fig. 2. It is shown that the calculated relative energies of most products and complexes are very close at the two levels and the five individual reactions (1a)–(3) are all exothermic reaction; the potential barriers are decreased by about 3 kcal/mol at the higher level. Fig. 2 also shows that the H-abstraction reaction from the halogenated-methyl group in chlorinated-acetaldehyde proceeds via a direct reaction mechanism, while H-abstraction from formyl position would form firstly hydrogen-bonded complex at the exit channel, which is more stable than the products by

about 2 kcal/mol at the CCSD(T)//MP2 level, followed by the dissociation to the products $\text{CH}_2\text{ClCO} + \text{HCl}$ or $\text{CHCl}_2\text{CO} + \text{HCl}$. Furthermore, the barrier heights for reactions (R1b) and (R2b) are higher than those for (R1a) and (R2a) about 5 kcal/mol, thus, the H-abstraction from $-\text{CHO}$ position dominate the two reactions. The corresponding potential barriers without ZPE corrections are 0.38, 1.45 and 1.86 kcal/mol, respectively, at the CCSD(T)//MP2 level for (R1a), (R2a), and (R3), and the ZPE corrected values are -1.14 , -0.81 , and -0.8 kcal/mol. If we use the formula $E_{a,298} = \Delta E^* + RT = V^* + \Delta \text{ZPE} + \Delta E(T) + RT$ as a simple estimation of the activation energy [28], where V^* and $\Delta E(T)$ represent the potential barrier height and thermal energy correction, the estimated activation energies are -0.98 , -0.65 , and -0.59 kcal/mol for the three reactions (R1a), (R2a), and (R3), respectively, which means that the title reactions are nearly barrierless, so they are expected to have larger rate constants.

3.2. Rate constants calculation

Dual-level dynamic calculations of the hydrogen abstraction reactions (R1)–(R3) are carried out with VTST-ISPE approach, in which six extra CCSD(T)/6-311+G(d,p)//MP2/cc-pVDZ energies are used to refine the classical energy profile obtained at the MP2 level. The rate constants are evaluated by the conventional transition state theory (TST) and the improved canonical variation transition state theory (ICVT) over a wide

Table 1

Calculated frequencies (cm^{-1}) of the stationary points at the MP2/cc-pVDZ and MPW1K/6-31+G(d,p) levels and experimental values

Species	Method	Frequencies
CH ₂ ClCHO	MP2	68, 290, 463, 721, 844, 1033, 1075, 1190, 1272, 1410, 1451, 1789, 2993, 3119, 3209
	MPW1K	31, 279, 479, 713, 852, 1075, 1083, 1238, 1320, 1445, 1477, 1918, 3067, 3175, 3248
CH ₂ ClCO	MP2	37, 262, 439, 754, 834, 914, 1147, 1259, 1421, 1941, 3115, 3196
	MPW1K	73, 268, 458, 776, 851, 946, 1181, 1310, 1457, 2039, 3162, 3239
CHClCHO	MP2	162, 274, 477, 548, 925, 1081, 1113, 1256, 1438, 2051, 2959, 3281
	MPW1K	194, 285, 491, 669, 937, 998, 1201, 1308, 1463, 1662, 3098, 3326
CHCl ₂ CHO	MP2	83, 260, 289, 325, 443, 773, 805, 1017, 1093, 1219, 1052, 1400, 1788, 3015, 3194
	MPW1K	83, 266, 280, 334, 458, 786, 826, 1059, 1118, 1262, 1297, 1438, 1926, 3098, 3264
CHCl ₂ CO	MP2	48, 259, 324, 368, 423, 788, 811, 921, 1199, 1249, 1998, 3158
	MPW1K	46, 265, 334, 368, 444, 812, 828, 955, 1248, 1295, 2045, 3215
CCl ₂ CHO	MP2	146, 205, 280, 292, 473, 696, 1038, 1075, 1179, 1423, 2164, 2971
	MPW1K	190, 216, 305, 348, 496, 706, 985, 1054, 1258, 1443, 1707, 3104
CCl ₃ CHO	MP2	85, 205, 253, 275, 324, 333, 451, 641, 769, 881, 1017, 1065, 1385, 1801, 3027
	MPW1K	84, 206, 257, 283, 332, 335, 469, 659, 789, 908, 1061, 1098, 1427, 1944, 3107
CCl ₃ CO	MP2	55, 187, 264, 268, 322, 396, 445, 592, 812, 851, 872, 2030
	MPW1K	60, 187, 271, 277, 330, 404, 468, 620, 834, 878, 913, 2066
HCl	MP2	3076
	MPW1K	3088
	Experimental	2991 ^a
TS1a	MP2	411i, 44, 55, 92, 275, 471, 674, 852, 950, 1045, 1187, 1267, 1290, 1447, 1830, 2041, 3124, 3216
TS1b	MP2	1284i, 58, 97, 122, 279, 406, 501, 758, 892, 960, 1065, 1080, 1147, 1231, 1415, 2683, 3044, 3199
TS2a	MP2	451i, 34, 53, 100, 261, 319, 321, 440, 793, 796, 926, 988, 1203, 1249, 1253, 1303, 2155, 3180
TS2b	MP2	1263i, 52, 82, 92, 212, 267, 269, 444, 469, 824, 860, 990, 998, 1049, 1074, 1383, 2244, 2992
TS3	MP2	635i, 34, 58, 103, 200, 264, 275, 324, 359, 449, 515, 788, 803, 923, 991, 1104, 1252, 2210
Complex-1	MP2	10, 32, 61, 108, 242, 293, 336, 445, 770, 837, 918, 1148, 1259, 1420, 1904, 2961, 3115, 3196
Complex-2	MP2	19, 25, 62, 69, 258, 259, 278, 345, 417, 426, 789, 816, 925, 1207, 1247, 1923, 2961, 3158
Complex-3	MP2	18, 24, 56, 70, 187, 241, 263, 273, 274, 326, 431, 448, 601, 816, 852, 881, 1946, 2977

^a From [24].

Table 2

Calculated enthalpies of formation at 298 K at the CCSD(T)/6-311+G(d,p)//MP2/cc-pVDZ level and the experimental references (in kcal/mol)

species	$\Delta H_{f,298}^0$	Experimental
CH ₂ ClCHO	-44.04 ± 0.36	-41.67 ± 1.05^a
CHCl ₂ CHO	-48.34 ± 0.36	
CCl ₃ CHO	-49.76 ± 0.36	-45.52 ± 2.96^a
CH ₂ ClCO	-4.12 ± 0.71	
CHClCHO	-3.08 ± 0.71	
CHCl ₂ CO	-5.90 ± 0.71	
CCl ₂ CHO	-8.81 ± 0.71	
CCl ₃ CO	-7.55 ± 0.71	-7.0^b

^a From [26].^b From [27].

temperature region from 220 to 2000 K. Tunneling is included by means of the small-curvature tunneling (SCT) correction. The calculated rate constants of these reactions together with the corresponding experimental data are displayed in Tables 4–6. From them, the variational effect is found for H-abstraction reactions (R1a) and

Table 3

The enthalpies of reactions (ΔH_{298}^0 in kcal/mol) calculated at the MP2/cc-pVDZ and CCSD(T)/6-311+G(d,p)//MP2/cc-pVDZ levels

Reactions	MP2/ cc-pVDZ	CCSD(T)// MP2
CH ₂ ClCHO + Cl → CH ₂ ClCO + HCl	−9.30	−9.38
→ CHClCHO + HCl	−1.99	−8.33
CHCl ₂ CHO + Cl → CHCl ₂ CO + HCl	−6.87	−6.86
→ CCl ₂ CHO + HCl	−3.81	−9.77
CCl ₃ CHO + Cl → CCl ₃ CO + HCl	−6.91	−7.08

(R2a), for example, the ratios of $k(\text{ICVT})/k(\text{TST})$ for (R1a) and (R2a) are 0.58 and 0.78 at 298 K, respectively. While for reactions (R1b), (R2b) and (R3), the TST values are almost same as the ICVT ones, implying that the variational effect is negligible. On the other hand, by contrasting the ICVT and ICVT/SCT, it is shown that they are asymptotic for (R1a) and (R2a) over the whole temperature range, but the SCT correction should be taken into account in the rate constant calculations for reactions (R1b) and (R2b) (H-abstraction from haloge-

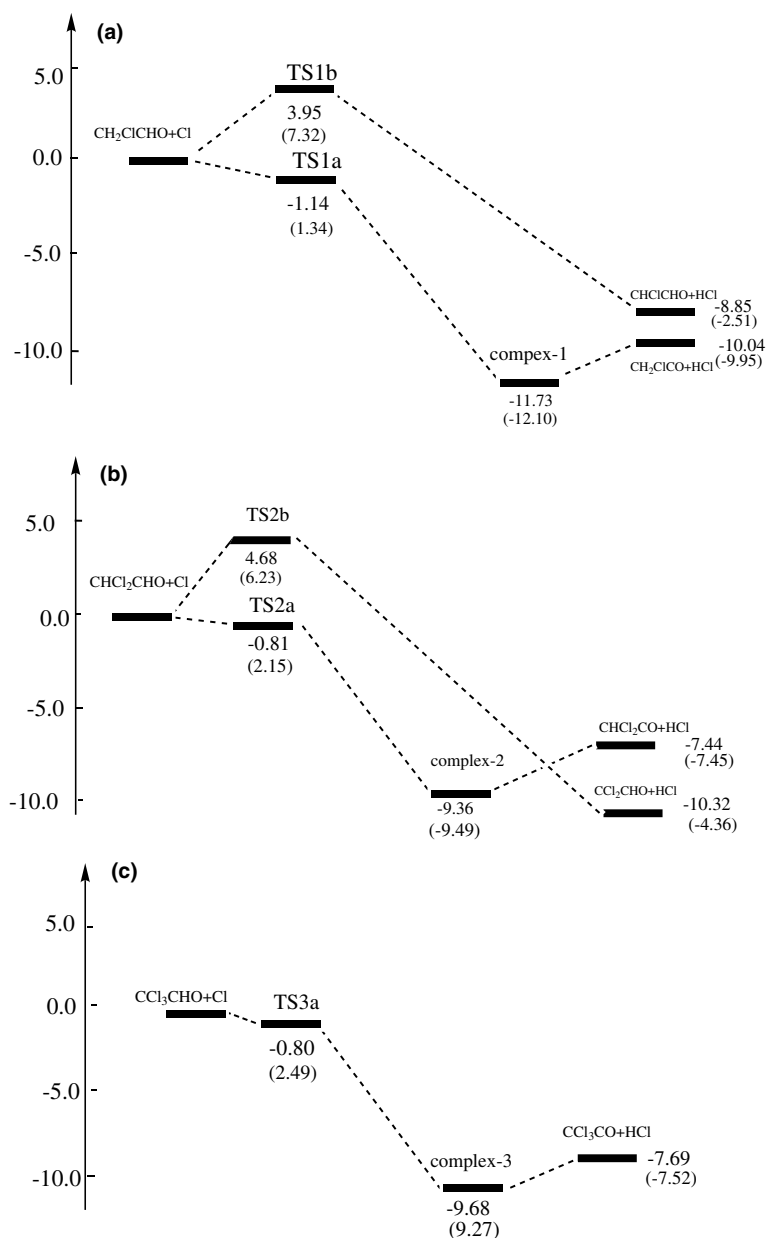


Fig. 2. Schematic pathways for the reactions: (a) $\text{CH}_2\text{ClCHO} + \text{Cl}$; (b) $\text{CHCl}_2\text{CHO} + \text{Cl}$; (c) $\text{CCl}_3\text{CHO} + \text{Cl}$. Relative energies with ZPE at the CCSD(T)/6-311+G(d,p)//MP2/cc-pVDZ level are in kcal/mol. The values in parentheses are those obtained at the MP2/cc-pVDZ level.

nated methyl group), and (R3) at low temperature range, with the $k(\text{ICVT}/\text{SCT})/k(\text{ICVT})$ ratios of 56.9, 2.6, and 2.0 at 220 K for (R1b), (R2b), and (R3), respectively.

The total rate constant for reactions (R1) and (R2) is obtained from the sum of the individual rate constants associated with the two channels. The temperature dependence of the total constant for the three reactions is present in Fig. 3(a)–(c), as well as the available experimental values; and the branching ratios for $\text{CH}_2\text{ClCHO} + \text{Cl}$ and $\text{CHCl}_2\text{CHO} + \text{Cl}$ is plotted in Fig. 4(a)–(b). It can be found from Figs. 3(a) and 4(a) that the total rate constant is almost equal to the value

of reaction channel 1a below 500 K, and the contribution of reaction channel 1b becomes important at high temperatures for (R1). The values of k_{1a}/k are 100%, 80%, and 61% at 298, 1000, and 2000 K, respectively. Similar observation can be found for reaction (R2). Thus for the multi-channel reactions (R1) and (R2), the dominant reaction channel is H-abstraction from formyl position leading to product CH_2ClCO and CHCl_2CO , respectively. In addition, Fig. 3(a) and (b) shows that the rate constants are almost temperature-independent for reactions (R1) and (R2) below 500 K, while in Fig. 3(c) there is slightly negative temperature dependent for reaction (R3) below 400 K.

Table 4

Calculated rate constants (in $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$) for the reaction $\text{CH}_2\text{ClCHO} + \text{Cl} \rightarrow \text{products}$ in the temperature range 220–2000 K at the CCSD(T)/6-311+G(d,p)/MP2/cc-pVDZ level of theory

T (K)	$\text{CH}_2\text{ClCHO} + \text{Cl} \rightarrow \text{CH}_2\text{ClCO} + \text{HCl}$			$\text{CH}_2\text{ClCHO} + \text{Cl} \rightarrow \text{CHClCHO} + \text{HCl}$			Total rate constants	Experimental
	TST	ICVT	ICVT/SCT	TST	ICVT	ICVT/SCT	ICVT/SCT	
220	2.35E – 11	1.70E – 11	1.71E – 11	1.90E – 16	1.60E – 16	9.10E – 15	1.71E – 11	$(1.5 \pm 0.3)\text{E} - 11^{\text{a}}$ $1.08\text{E} - 11^{\text{b}}$
250	2.56E – 11	1.68E – 11	1.69E – 11	6.81E – 16	5.58E – 16	1.43E – 14	1.69E – 11	
270	2.70E – 11	1.68E – 11	1.69E – 11	1.38E – 15	1.20E – 15	1.92E – 14	1.69E – 11	
298	2.92E – 11	1.70E – 11	1.71E – 11	3.24E – 15	2.81E – 15	2.85E – 14	1.71E – 11	
400	3.81E – 11	1.85E – 11	1.86E – 11	2.92E – 14	2.52E – 14	9.62E – 14	1.87E – 11	
500	4.77E – 11	1.89E – 11	1.89E – 11	1.18E – 13	1.00E – 13	2.42E – 13	1.91E – 11	
800	8.05E – 11	1.98E – 11	1.99E – 11	1.29E – 12	1.06E – 12	1.51E – 12	2.14E – 11	
1000	1.05E – 10	2.19E – 11	2.19E – 11	3.28E – 12	2.66E – 12	3.34E – 12	2.52E – 11	
1200	1.32E – 10	2.49E – 11	2.49E – 11	3.51E – 12	5.23E – 12	6.14E – 12	3.10E – 11	
1500	1.77E – 10	3.04E – 11	3.04E – 11	1.39E – 11	1.08E – 11	1.20E – 11	4.24E – 11	
1800	2.25E – 10	3.69E – 11	3.69E – 11	2.45E – 11	1.86E – 11	2.00E – 11	5.69E – 11	
2000	2.60E – 10	4.16E – 11	4.16E – 11	3.33E – 11	2.50E – 11	2.65E – 11	6.81E – 11	

^a From [7].

^b From [6].

Table 5

Calculated rate constants (in $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$) for the reaction $\text{CHCl}_2\text{CHO} + \text{Cl} \rightarrow \text{products}$ in the temperature range 220–2000 K at the CCSD(T)/6-311+G(d,p)/MP2/cc-pVDZ level of theory

T (K)	$\text{CHCl}_2\text{CHO} + \text{Cl} \rightarrow \text{CHCl}_2\text{CO} + \text{HCl}$			$\text{CHCl}_2\text{CHO} + \text{Cl} \rightarrow \text{CHCl}_2\text{CHO} + \text{HCl}$			Total rate constants	Experimental
	TST	ICVT	ICVT/SCT	TST	ICVT	ICVT/SCT	ICVT/SCT	
220	1.06E – 11	4.74E – 12	5.58E – 12	1.31E – 17	1.30E – 17	3.38E – 17	5.58E – 12	$12.7\text{E} - 12^{\text{a}}$ $(13 \pm 2)\text{E} - 12^{\text{b}}$
250	8.61E – 12	5.04E – 12	5.72E – 12	5.74E – 17	5.72E – 17	1.20E – 16	5.72E – 12	
270	7.79E – 12	5.22E – 12	5.81E – 12	1.30E – 16	1.3E – 16	2.45E – 16	5.81E – 12	
298	7.04E – 12	5.47E – 12	5.97E – 12	3.48E – 16	3.47E – 16	5.84E – 16	5.97E – 12	
400	6.11E – 12	5.68E – 12	5.96E – 12	4.38E – 15	4.37E – 15	5.83E – 15	5.97E – 12	
500	6.28E – 12	5.99E – 12	6.18E – 12	2.16E – 14	2.16E – 14	2.6E – 14	6.21E – 11	
800	8.72E – 12	8.44E – 12	8.54E – 12	3.22E – 13	3.21E – 13	3.46E – 13	8.89E – 12	
1000	1.12E – 11	1.08E – 11	1.09E – 11	9.16E – 13	9.14E – 13	9.58E – 13	1.19E – 11	
1200	1.41E – 11	1.37E – 11	1.38E – 11	1.97E – 12	1.97E – 12	2.03E – 12	1.58E – 11	
1500	1.93E – 11	1.87E – 11	1.88E – 11	4.59E – 12	4.58E – 12	4.68E – 12	2.35E – 11	
1800	2.53E – 11	2.45E – 11	2.46E – 11	8.60E – 12	8.57E – 12	8.7E – 12	3.33E – 11	
2000	2.97E – 11	2.88E – 11	2.88E – 11	1.21E – 11	1.20E – 11	1.22E – 11	4.10E – 11	

^a From [6].

^b From [7].

By comparing the theoretical rate constants with the experimental ones, we can see the agreement between them is good. The factors of deviation between the calculated and experimental data [6–9] are within 2. For the reaction $\text{CH}_2\text{ClCHO} + \text{Cl}$, the ICVT/SCT rate constant is slightly higher than the two measured results [6,7] at 298 K, while for the reactions $\text{CHCl}_2\text{CHO} + \text{Cl}$ and $\text{CCl}_3\text{CHO} + \text{Cl}$, the calculated results underestimate the experimental values [6–9]. In particular, with respect to the reaction $\text{CCl}_3\text{CHO} + \text{Cl}$, the latest determined values by Platz et al. [8] and Talukdar et al. [9] are lower than those by Starcke et al. [6] and Scollard et al. [7], while our calculated results show better agreement with the formers. Also, the theoretical rate constants decrease in the order of $k_1 > k_2 > k_3$, thus, the reactivity decreases substantially with chloride substitution at the methyl

position of acetaldehydes. We find, however, halogenation does not lead to significant changes in the C–H bond energies (D_{298}^0), with the D_{298}^0 values of 87.5, 89.9, 89.8 kcal/mol for CH_2ClCHO , CHCl_2CHO and CCl_3CHO at the –CHO group. These results mean that the relatively large decrease in reactivity upon substitution are mainly a consequence of polar effects in the transition states.

Since there is few data available at other temperature, for convenience of future experimental measurements, the three-parameter fits for the ICVT/SCT rate constants for the title reactions within 220–2000 K give the expressions as follows (in $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$):

$$k_1 = 9.82 \times 10^{-16} T^{1.42} \exp(484.7/T);$$

Table 6

Calculated rate constants (in $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) for the reaction $\text{CCl}_3\text{CHO} + \text{Cl} \rightarrow \text{CCl}_3\text{CO} + \text{HCl}$ in the temperature range 220–2000 K at the CCSD(T)/6-311+G(d,p)//MP2/cc-pVDZ level of theory

T (K)	$\text{CCl}_3\text{CHO} + \text{Cl} \rightarrow \text{CCl}_3\text{CO} + \text{HCl}$			Experimental
	TST	ICVT	ICVT/SCT	
220	$2.00\text{E} - 12$	$1.76\text{E} - 12$	$3.58\text{E} - 12$	
250	$1.95\text{E} - 12$	$1.82\text{E} - 12$	$3.21\text{E} - 12$	
270	$1.96\text{E} - 12$	$1.87\text{E} - 12$	$3.06\text{E} - 12$	
298	$1.99\text{E} - 12$	$1.94\text{E} - 12$	$2.93\text{E} - 12$	$5.4\text{E} - 12^{\text{a}}$ $6.0\text{E} - 12^{\text{b}}$ $7.1\text{E} - 12^{\text{c}}$ $9.0\text{E} - 12^{\text{d}}$
400	$2.34\text{E} - 12$	$2.32\text{E} - 12$	$2.94\text{E} - 12$	
500	$2.86\text{E} - 12$	$2.85\text{E} - 12$	$3.33\text{E} - 12$	
800	$5.22\text{E} - 12$	$5.20\text{E} - 12$	$5.54\text{E} - 12$	
1000	$7.34\text{E} - 12$	$7.31\text{E} - 12$	$7.61\text{E} - 12$	
1200	$9.85\text{E} - 12$	$9.81\text{E} - 12$	$1.01\text{E} - 11$	
1500	$1.43\text{E} - 11$	$1.42\text{E} - 11$	$1.45\text{E} - 11$	
1800	$1.95\text{E} - 11$	$1.94\text{E} - 11$	$1.97\text{E} - 11$	
2000	$2.33\text{E} - 11$	$2.32\text{E} - 11$	$2.35\text{E} - 11$	

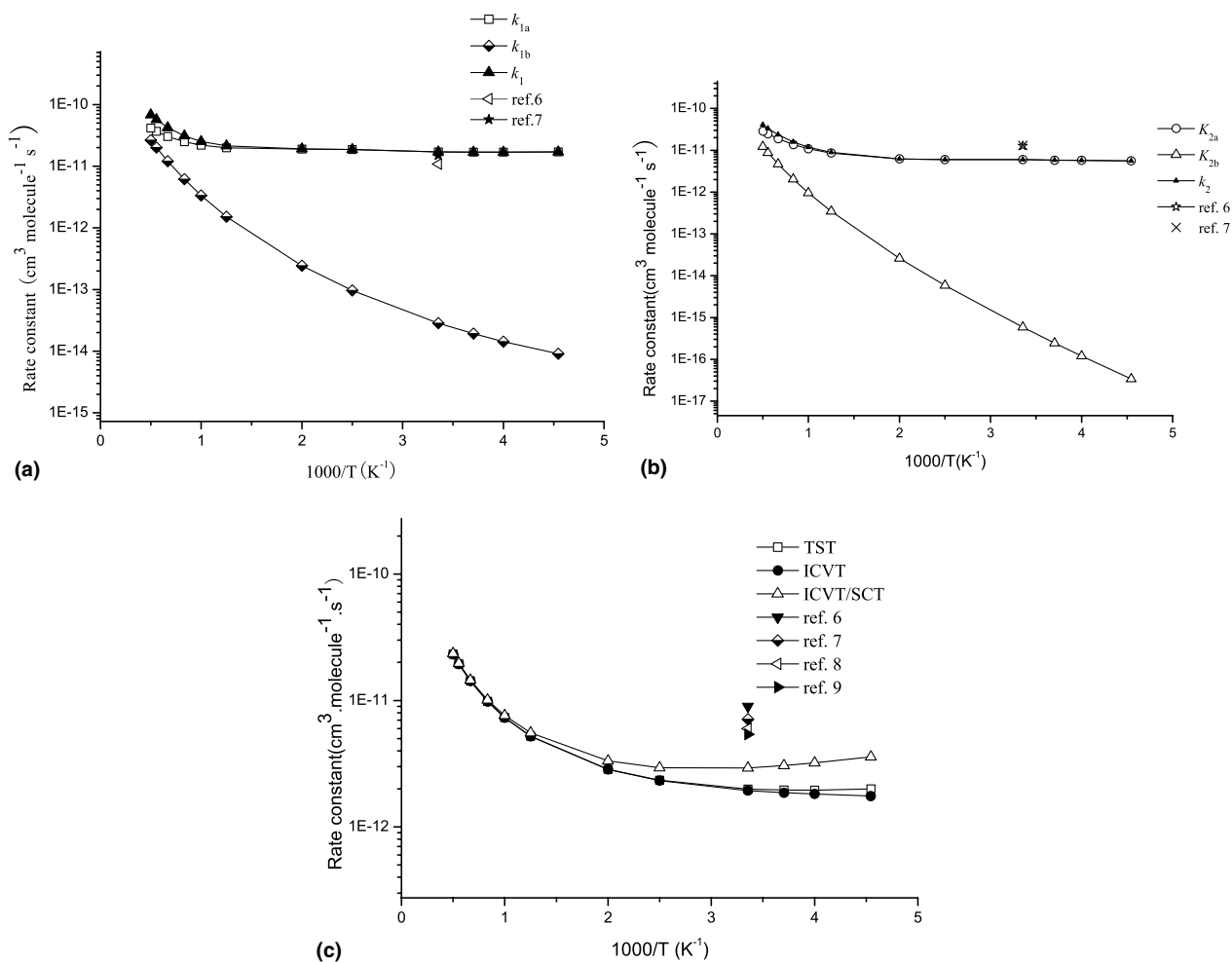
^a From [9].^b From [8].^c From [7].^d From [6].

Fig. 3. The total rate constants k and available experimental values ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) as functions of the reciprocal of the temperature (K) over the temperature range 220–2000 K: (a) for reaction $\text{CH}_2\text{ClCHO} + \text{Cl} \rightarrow \text{products}$; (b) for reaction $\text{CHCl}_2\text{CHO} + \text{Cl} \rightarrow \text{products}$; (c) for reaction $\text{CCl}_3\text{CHO} + \text{Cl} \rightarrow \text{products}$.

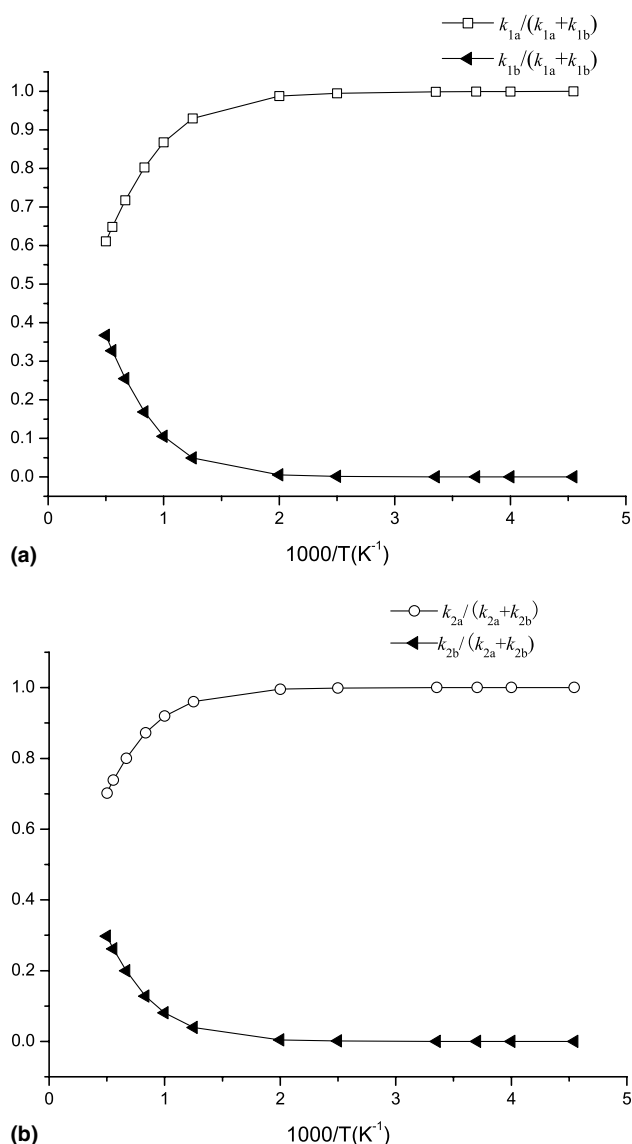


Fig. 4. Calculated branching ratios vs. $1000/T$ between 220 and 2000 K: (a) for reaction $CH_2ClCHO + Cl \rightarrow \text{products}$; (b) for reaction $CHCl_2CHO + Cl \rightarrow \text{products}$.

$$k_2 = 5.20 \times 10^{-18} T^{2.04} \exp(669.0/T);$$

$$k_3 = 8.82 \times 10^{-19} T^{2.20} \exp(732.9/T).$$

4. Conclusions

In this paper, a direct ab initio dynamics method is employed to study the hydrogen abstraction reactions $CH_{3-n}Cl_nCHO + Cl$ ($n = 1-3$). For the reactions $CH_2ClCHO + Cl \rightarrow \text{products}$ and $CHCl_2CHO + Cl \rightarrow \text{products}$, two H-abstraction reaction channels are identified. For each reaction, the theoretical rate constants are calculated in the temperature range from 220 to 2000 K by the improved canonical variational transition

state theory (ICVT) with a small-curvature tunneling correction (SCT) at the CCSD(T)/6-311+G(d,p)//MP2/cc-pVDZ level, and the results are well consistent with the experimental values. The calculated results show that the reactivity decreases from CH_2ClCHO through $CHCl_2CHO$ to CCl_3CHO , and for the title reactions H-abstraction from the formyl position is the major reaction channel, while H-abstraction from halo-genated-methyl position may play a role with the temperature increasing. Furthermore, in order to further reveal the thermodynamics properties, the enthalpies of formation of CH_2ClCHO , $CHCl_2CHO$, CCl_3CHO , and CH_2ClCO , $CHClCHO$, $CHCl_2CO$, CCl_2CHO , CCl_3CO are studied using the isodesmic reactions.

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