Theoretical study of neighboring group participation of methyl ω-chloroesters elimination kinetics in the gas phase

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The mechanisms of the homogeneous, unimolecular, gas-phase elimination kinetics of several methyl ω-chloroesters were examined by using the 'ab initio' and DFT level of theories. Theoretical calculations of dehydrochlorination of methyl 3-chloropropionate suggest a planar concerted, non-synchronous, four-membered cyclic transition state to give methyl acrylate. However, the parallel competitive gas-phase elimination of methyl 4-chlorobutyrate and methyl 5-chlrovalerate occurs through neighboring group participation to render methyl chloride and the corresponding lactone through a concerted, semi-polar five- and six-membered cyclic transition state type of mechanism. Calculated thermodynamic and kinetic parameters reasonably agree with the experimental values at DFT B3LYP/6-31G* theory level. Geometrical parameters, NBO charges and bond indexes showed strong polarization at $C^{\delta+}\cdots Cl^{\delta-}$ bond in the transition state suggesting the breaking of C—Cl bond as rate-determining factor for both dehydochlorination and lactone formation reactions. The synchronicity parameters suggest a concerted polar mechanism implying a TS which has ion-pair character for lactone product formation. Copyright © 2008 John Wiley & Sons, Ltd.

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INTRODUCTION

The homogeneous, unimolecular gas-phase pyrolysis or elimination of simple alkyl halides are generally known to give the corresponding olefin and hydrogen halide as described in reaction (1).[1–5]

$$R^1R^2C\!\!-\!\!CR^3R^4 \longrightarrow R^1R^2C\cdots CR^3R^4 \longrightarrow R^1R^2C\!\!=\!\!CR^3R^4 + HX \quad (1)$$
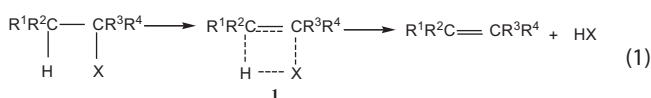
According to experimental data, the commonly accepted mechanism consisted of a concerted four-membered cyclic transition state structure **(1)**. For molecular elimination of HX, the presence of a β-hydrogen adjacent to the C—X bond is necessary.

In 1955, Maccoll and Thomas[6] were able to show a good correlation between activation energy for elimination and the heterolytic bond dissociation energies of the C—X bond. In view of these results, they suggested transition state mechanism **(2** Scheme 1) where activation is favored by polarization of the C—X bond, in the direction of $C^{\delta+}\cdots X^{\delta-}$, with some assistance from the adjacent C—H bond. A few years later, Benson and Bose[7] proposed a semi-ion pair transition state mechanism (**3** Scheme 1) for the pyrolysis for simple organic halides. Along this line of work and on the basis of this model (**3** Scheme 1), Benson and O'Neal[8] have presented calculations of energies and entropies of activation which were in good agreement with the experimental values.

In 1967, Maccoll and Thomas[9] considered a very polar transition state in terms of an intimate ion-pair intermediate

(**4** Scheme 1) and presented several evidences in support of this idea: (a) the activation energies decreased while the rates increased by α-substitution with electron-releasing groups, (b) electron-releasing substituents at the β-position of the C—X bond gives small increase in rates, (c) as described above,[6] there is a strong correlation between energies of activation and the heterolytic bond dissociation energies, (d) a characteristic feature of positive carbon ion behavior in solution, such as the Wagner-Meerwein rearrangement, has been described in the gas-phase pyrolysis of neopentyl chloride[10,11] and isobornyl chlorides,[12,13] (e) a similarity charged transition state or intermediate appears to take place in the gas-phase pyrolysis and in nucleophilic substitution (S_N1) and elimination reactions (E1) in polar solvents.

Lactonization of ethyl γ-bromobutyrate at 200 °C was found to occur in various media.[14] [reaction (2)]. However, there was no reaction in the gas phase and only HBr elimination at 450 °C was described. The formation of HBr at 450 °C was considered to be surprising because the ethyl group of the ester should have

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eliminated, as ethylene, more easily than the dehydrobromination process.

(2)
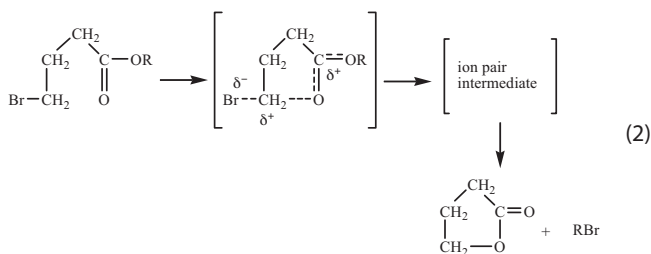
This fact led to investigate the homogenous, unimolecular elimination kinetics of methyl ω-chloroesters in the gas phase,[15,16] where the oxygen carbonyl of the $COOCH_3$ group was found to assist anchimerically the methyl 4-chlorobutyrate and methyl 5-chlorovalerate. This consideration was verified by the fact that besides HCl formation, ring-closed products were also obtained [reaction (3)].

(3)
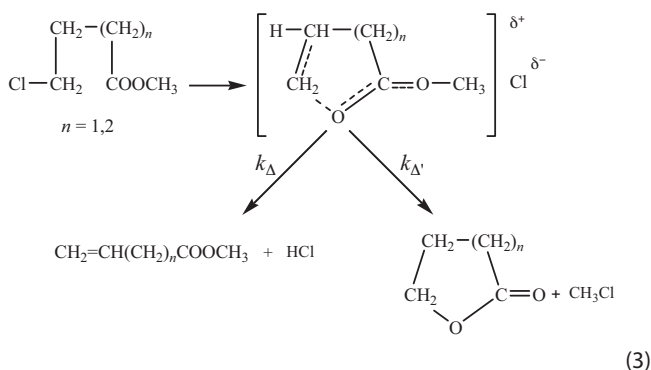
The mechanisms of these eliminations [(reaction 3)] were explained in terms of an intimate ion-pair mechanism, involving a neighboring $COOCH_3$ group participation and an intramolecular solvation or autosolvation of the chloride ion, which may proceed in two parallel reactions giving the corresponding unsaturated methyl ester and the lactone products.

An interesting parallel elimination of methyl 4-chlorobutyrate and methyl 5-chlorovalerate is the formation CH_3Cl and the corresponding lactone [(reaction (3)]. This mechanistic consideration of intramolecular solvation or autosolvation may possible find some support by theoretical calculations. Consequently, the present work aimed at examining the calculation of the kinetic parameters and the characterization of the potential energy surface (PES) for the gas-phase elimination of the above-mentioned methyl ω-chloroesters. The present theoretical calculations may also provide some evidence of Maccoll's idea[1,9] that intimate ion-pair mechanism is possible in gas-phase pyrolysis of some types of organic halides.

COMPUTATIONAL METHODS AND MODELS

A theoretical study on the mechanism of hydrogen chloride formation from methyl 3-chloropropionate, and the lactone-forming parallel reaction for methyl 4-chlorobutyrate and methyl 5-chlrovalerate was carried out at B3LYP/6-31G*, MP2//6-31G, and MP2/6-31G* levels of theory as implemented in Gaussian 98.[17] The Berny standard algorithm was used for analytical gradient optimization routines with convergence on the density matrix was 10^{-9} atomic units, the threshold value for maximum

displacement was 0.0018 Å, and that for the maximum fore was 0.00045 Hartree/Bohr. Transition states search was performed using Quadratic Synchronous Transit protocol. Optimized geometries for reactants, products, and transition states structures at each theory level were characterized by using frequency by means of normal-mode analysis. Intrinsic reaction coordinate (IRC) calculations were performed to verify transition state structures.

Thermodynamic quantities such as zero point vibrational energy (ZPVE), temperature corrections ($E(T)$), and absolute entropies ($S(T)$), were obtained from frequency calculations and consequently, the rate coefficient can be estimated assuming that the transmission coefficient is equal to 1. Temperature corrections and absolute entropies were obtained assuming ideal gas behavior from the harmonic frequencies and moments of inertia by standard methods[18] at average temperature and pressure values within the experimental range. Scaling factors for frequencies and zero point energies for the methods used are taken from the literature.[19]

Method	f VIB	fZPE
B3LYP/6-311G(D,P)	0.97	0.99
MP2(Full)/6-31G(D)	0.9427	0.9676

The classical TST[20–22] was used to calculate rate coefficients $k(T)$ assuming that the transmission coefficient is equal to 1, as expressed in the following expression:

$$k(T) = (KT/h) \exp(-\Delta G^{\#}/RT)$$

where $\Delta G^{\#}$ is the Gibbs free energy change between the reactant and the transition state and K, h are the Boltzman and Plank constants respectively.

$\Delta G^{\#}$ was calculated using the following relations:

$$\Delta G^{\#} = \Delta H^{\#} - T\Delta S^{\#}$$

$$\Delta H^{\#} = V^{\#} + \Delta ZPVE + \Delta E(T)$$

where $V^{\#}$ is the potential energy barrier and $\Delta ZPVE$ and $\Delta E(T)$ are the differences of ZPVE and temperature corrections between the TS and the reactant, respectively.

RESULTS AND DISCUSSION

Kinetic and thermodynamic parameters

The elimination of hydrogen chloride from methyl 3-chloropropionate showed to occur in a concerted process through a quasi-planar four-membered transition state. With respect to methyl 4-chlorobutyrate and methyl 5-chlrovalerate, the parallel elimination reactions rendering the corresponding lactone and methyl chloride occur through a concerted, semi-polar five- and six-membered cyclic transition state type of mechanism. The dehydrochlorination of these substrates shows a similar barrier to lactone formation, suggesting these reactions occur in parallel competitive fashion. For methyl 4-chlorobutyrate and methyl 5-chlorovalerate dehydochlorination barriers are 230 and 228

Table 1. Kinetic and thermodynamic parameters of methyl ω-chloroesters at 450 °C (723 K) and 0.186184 atm

| Method	Ea (kJ/mol)	Log A (s^{-1})	$10^4 k_1$ (s^{-1})	($H^{\neq}$(kJ mol^{-1})	($S^{\neq}$(J mol^{-1} K^{-1})	($G^{\neq}$(kJ mol^{-1})
Methyl 3-chloropropionate	dehydrochlorination					
Experimental	231.5	13.22	3.1	225.5	−7.51	230.9
B3LYP/ 6-31G*	228.5	13.61	12.6	222.4	−0.11	222.5
B3LYP/ 6-31G**	220.1	13.56	45.1	214.1	−1.010	214.9
B3LYP/ 6-31+G**	215.7	13.58	99.9	209.7	−0.585	210.1
MP2/6-31G	249.7	13.77	0.5	243.7	3.04	241.5
MP2/6-31G*	283.6	13.85	0.002	277.6	4.54	274.3
Methyl 4-chlorobutyrate	lactone formation					
Experimental	223.0	12.82	5.1	217.0	−3.63	214.2
B3LYP/ 6-31G*	224.1	12.89	4.9	218.1	−13.86	228.2
B3LYP/ 6-31G**	221.8	12.84	0.7	215.8	−14.79	226.5
B3LYP/ 6-31+G**	215.3	12.85	2.0	209.3	−14.54	219.8
MP2/6-31G	231.6	12.91	1.5	225.6	−13.54	235.3
RHF/6-31G*	219.2	12.61	6.0	213.2	−19.13	227.0
Methyl 4-chlorobutyrate	dehydrochlorination					
Experimental	224.3	13.23	9.1	219.2	7.3	224.5
B3LYP/ 6-31G*	230.0	14.21	39.2	224.0	11.4	215.7
Methyl -5-chlorovalerate	lactone formation					
Experimental	226.2	12.83	3.00	220.2	−15.17	231.2
B3LYP/ 6-31G*	212.4	12.56	16.35	206.4	−20.13	221.0
B3LYP/ 6-31G**	210.1	12.56	23.99	204.1	−20.13	218.7
B3LYP/ 6-31+G**	201.6	12.48	81.62	195.6	−21.71	211.3
RHF/6-31G*	205.3	12.91	11.88	199.3	−13.54	209.0
Methyl -5-chlorovalerate	dehydrochlorination					
Experimental	226.2	12.83	3.09	220.2	−14.97	231.0
B3LYP/ 6-31G*	228.4	14.20	49.88	222.4	11.32	214.3
Experimental data from references [15,16]						

respectively, compared to 224 and 212 kJ/mol at B3LYP/ 6-31G* level, respectively.

Calculated thermodynamic and kinetic parameters are reported in Table 1. The results demonstrate that B3LYP/6-31G* results are in better agreement to the experimental values compared to MP2 method. The use of polarization functions was important in DFT calculations; however inclusion of diffuse function did not improve the results. MP2 method gave consistently higher barriers compared to experimental data and the use of polarization functions did not recover better parameters. RHF estimations for thermodynamics and kinetic parameters always gave low barriers due to the non inclusion of correlation energy as expected; however, the geometries are very similar in all methods.

Transition state and mechanism

The optimized TS structures for the three substrates are shown in Fig. 1, Scheme 2. All TS were verified by analysis of the unique imaginary frequency and by IRC calculations. In the case of methyl 3-chloropropionate, dehydrochlorination is the sole reaction observed. The TS was found to be intermediate in the reaction coordinate, and almost planar in configuration. For methyl 4-chlorobutyrate and methyl 5-chlorovalerate, the parallel reaction of lactone formation also occurs, and the TS is late in the reaction coordinate. The IRC calculations gave a configuration for the reactant that is higher in energy than the optimized reactant, suggesting that the substrate adopts a reactive-high energy conformation prior to the reaction for methyl 4-chloro butyrate and methyl 5-chlorovalerate (Fig. 2). The hydrogen chloride elimination of these substrates shows a TS similar to that observed for methyl 3-chloropropionate. In the case of HCl elimination, the TS display the carbonyl oxygen is in position for anchimeric assistance behind the C—Cl bond for all substrates (in Fig. 1, TS for HCl elimination from methyl 3-chloropropionate, top structure). The parallel reaction observed for methyl 4-chloro butyrate and methyl 5-chlorovalerate also showed participation of the carbonyl oxygen to the exit of Cl atom, while the methyl is still bonded to the ester oxygen, forming a TS configuration similar to the lactone intermediate.
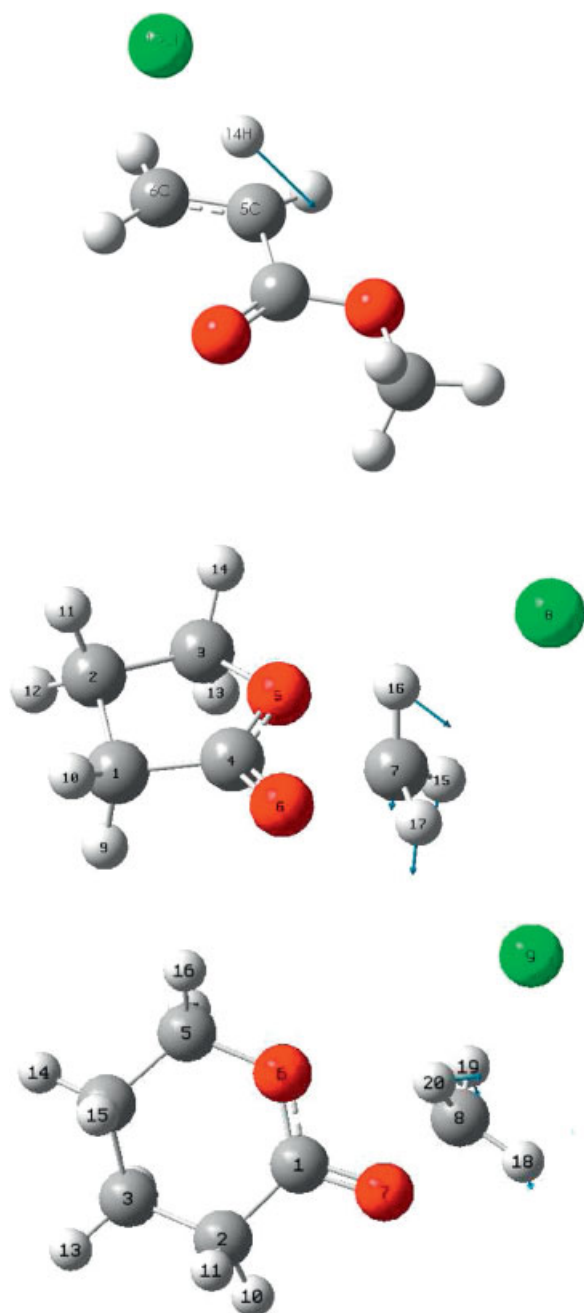
Figure 1. Optimized transition state structures for HCl elimination from methyl 3-chloropropionate (top), lactone formation from methyl 4-chlorobutyrate (center), and methyl 5-chlorovalerate (bottom).

Scheme 1.

The geometrical parameters for the TS reactant and product are given in Tables 2a–c; atom numbering is according to Scheme 2. Parameters are reported for HCl elimination from mehyl 3-chloropopionate and lactone formation from methyl 4-chlorobutyrate and methyl 5-chlorovalerate. In the three cases, the C—Cl is very elongated in the TS, however, in the case of the TS for lactone forming molecules, the bond dissociation is practically complete suggesting an intimate ion-pair configuration. For methyl 3-chloropropionate, the TS is almost planar as seen in dihedral 1.025. The TS for lactone formation from methyl
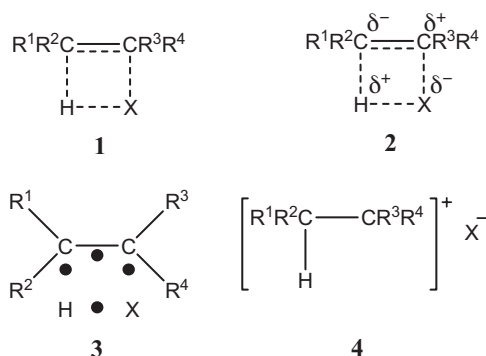
4-chlorobutyrate and methyl 5-chlorovalerate is late and showed deviations from planarity. The carbonyl oxygen assisting is very close to the carbon bearing the chlorine in the latter substrates showing an advanced lactone formation as illustrated by C_5—C_3 distance for methyl 4-chlorobutyrate (1.471 in the TS) and O_6—C_5 for methyl 5-chlorovalerate (1.471 in the TS). The TSs were verified by means of IRC calculations which also provided intermediate structures showing the reaction path leading to lactone formation.

Calculated NBO charges are given in Tables 3a–c. Considering methyl 3-chloropropionate, the TS charges reveal an increase in electron density at Cl_{13} (-0.47429) while C_6 becomes more positive (from -0.42139 in the reactant to -0.09947 in the TS), also H_{14} is positively charged in the TS (0.35023). Analysis of NBO charges for methyl 4-chlorobutynate and methyl 5-chlorovalerate shows a much augmented negative charge at Cl_8 (-0.809) and Cl_9 (-0.835) in the TS, respectively, while electron density at the carbon atoms supporting the chlorine in the reactants (C_3 and C_5 respectively) is diminished. The oxygen atoms forming the lactone ring (O_5 and O_6 respectively) are less negatively charged compared to the reactants, implying a displacement of electron density from the oxygen to the carbon bearing the chlorine in assistance to its exit in the elimination process. Charge separation Cl—C is bigger for methyl 4-chlorobutynate and methyl 5-chlorovalenate in the TS, supporting the intimate ion-pair idea.

Bond order analysis

NBO calculations had been successfully used to estimate bond orders describing reaction changes.[23–25] The Wiberg bond indexes[26] were computed using the natural bond orbital NBO program[27] as implemented in Gaussian 98W. Bond formation and bond breaking involved in the reaction mechanism can be monitored by means of the Synchronicity (Sy) concept proposed by Moyano *et al.*[28] defined by the expression:
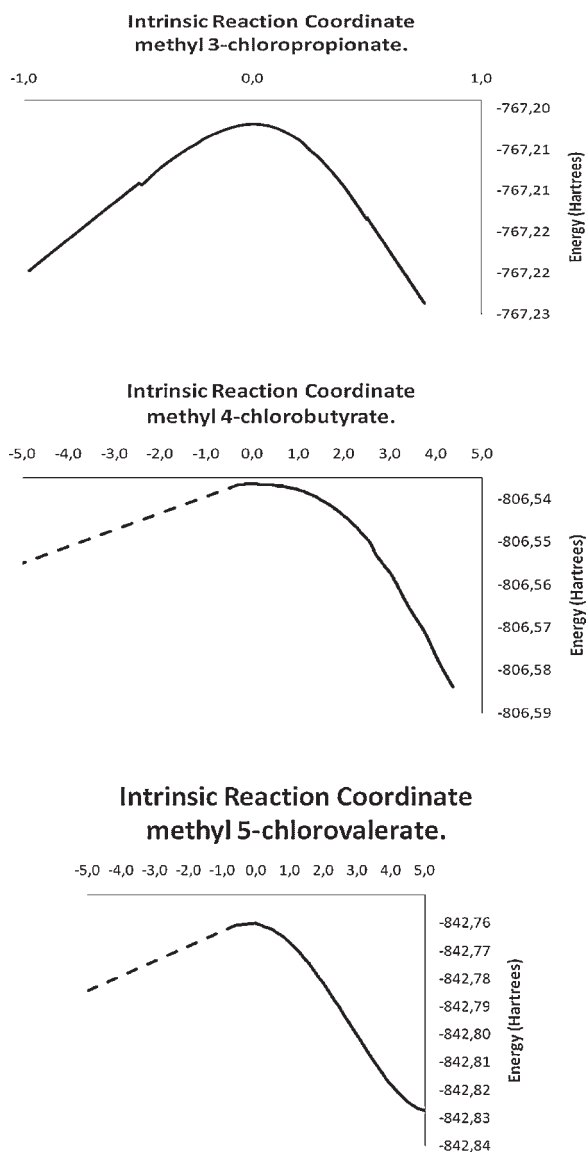
$$Sy = \frac{1 - \left[\sum_{i=1}^{n} |\delta Bi - \delta Bav| / \delta Bav\right]}{2n - 2}$$

where n represents the number of bonds directly involved in the reaction and the relative variation of the bond index is obtained from

$$\delta B_i = \frac{[B_i^{TS} - B_i^{R}]}{[B_i^{P} - B_i^{R}]}$$
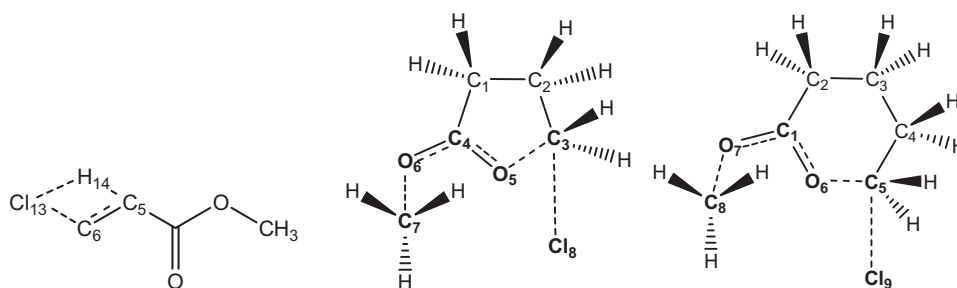
Scheme 2. Drawings of the TS for 3-methylpropionate (left), 4-methylbutyrate (center), and 5-chlrorovalerate (right) in the gas-phase elimination reaction of hydrogen chloride

Figure 2. Intrinsic reaction coordinate calculation (IRC) plots for methyl 3-chloro propionate (top), methyl 4-chlorobutyrate (center), and methyl 5-chlorovalerate (bottom). The TS lead to a higher energy configuration of the reactant for the parallel reaction in lactone forming compounds from methyl 4-chlorobutyrate and methyl 5-chlorovalerate, implying the need for structure rearrangement prior to the reaction in this path

where the superscripts R, TS, P, represent reactant, transition state, and product respectively. The evolution in bond change is calculated as

$$\%Ev = \delta B_i * 100$$

The average value is calculated from

$$\delta B_{ave} = 1/n \sum_{i=1}^{n} \delta B_i$$

Bonds indexes were calculated for those bonds involved in the reaction changes, that is: $C_6—Cl_{13}$, $C_6—C_5$, $C_5—H_{14}$, $H_{14}—Cl_{13}$, for methyl 3-chloropropionate; $C_7—O_6$, $O_6—C_4$, $C_4—O_5$, $O_5—C_3$, $Cl_8—C_3$, $Cl_8—C_7$ for methyl 4-chlorobutyrate, and $C_8—O_7$, $O_7—C_1$, $C_1—O_6$, $O_6—C_5$, $C_5—Cl_9$, $Cl_9—C_8$, for methyl 5-chlorovalerate, the remaining bonds stay practically unaltered during the process.

Bond order data from NBO calculations for the elimination reaction are given in Tables 4a–c. In all cases, the most advanced reaction coordinate is the breaking of C—Cl bond. However, for the substrates forming the lactone intermediate this effect is more important being close to 100% in the TS structure compared to ≅61% for methyl 3-chloropropionate. In the latter, the second most advanced coordinate is the breaking of $C_5—H_{14}$ bond, with intermediate progress in other events. Considering lactone forming substrates, the second most advanced coordinate is $O_5—C_3$ and $O_6—C_5$ for methyl 4-chlorobutyrate and methyl 5-chlorovalerate, respectively, suggesting late TS close to the lactone configuration. The evolution observed for $O_6—C_5$ and $C_1—O_6$ for methyl 4-chlorobutyrate and methyl 5-chlorovalerate, respectively, is also important. These data suggest late TS for the lactone forming compounds with bonds being similar to those in the intermediate. Conversely, the TS configuration of methyl 3-chloropropionate is more intermediate in the reaction coordinate.

Table 2a. Geometrical parameters reactant, TS and products for methyl 3-chloropropionate dehydrochlorination

	$C_6—Cl_{13}$	$C_6—C_5$	$C_5—H_{14}$	$H_{14}—Cl_{13}$	D (Cl—C—C—H)
Reactant	1.8153	1.5224	1.0959	2.9407	58.859
TS	2.5947	1.4030	1.2941	1.7692	1.025
Product	3.8015	1.3376	2.5991	1.2968	2.124

Distances are in Angstroms, dihedral in degrees.

Table 2b. Geometrical parameters reactant, TS and products for methyl 4-chlorobutyrate lactone formation

	C_7—O_6	O_6—C_4	C_4—O_5	O_5—C_3	Cl_8—C_3	Cl_8—C_7	D (O_5—C_4—O_6—C_7)	D (C_4—O_6—C_7—Cl_8)
Reactant	1.417	1.322	1.188	3.834	1.799	4.743	0.88	62.47
TS	1.558	1.257	1.307	1.471	5.778	2.865	10.24	53.14
Product	3.238	1.182	1.334	1.422	6.532	1.793	0.90	5.90

Distances are in Angstroms, dihedrals in degrees.

Table 2c. Geometrical parameters reactant, TS and products for methyl 5-chlorovalerate lactone formation

	C_8—O_7	O_7—C_1	C_1—O_6	O_6—C_5	C_5—Cl_9	Cl_9—C_8	D (O_6—C_1—O_7—C_8)	D (C_1—O_7—C_8—Cl_9)
Reactant	1.440	1.356	1.211	4.071	1.824	4.432	0.75	70.49
TS	1.555	1.266	1.298	1.471	5.482	2.867	9.69	39.40
Product	3.153	1.209	1.359	1.448	6.106	1.812	−1.48	−3.64

Distances are in Angstroms, dihedrals in degrees.

Table 3a. NBO charges reactant, TS and products for methyl 3-chloropropionate gas-phase elimination

	Cl_{13}	C_6	C_5	H_{14}
Reactant	−0.08844	−0.42139	−0.57966	0.27253
TS	−0.47429	−0.09947	−0.64170	0.35023
Products	−0.29434	−0.35975	−0.34765	0.27561

Table 3b. NBO charges reactant, TS and products for methyl 4-chlorobutyrate gas-phase elimination

	C_7	O_6	C_4	O_5	C_3	Cl_8
Reactant	−0.336	−0.547	0.832	−0.603	−0.414	−0.429
TS	−0.378	−0.454	0.877	−0.470	−0.116	−0.809
Products	−0.650	−0.574	0.825	−0.550	−0.116	−0.110

Table 3c. NBO charges reactant, TS and products for methyl 5-chlorovalerate gas-phase elimination

	C_8	O_7	C_1	O_6	C_5	Cl_9
Reactant	−0.326	−0.558	0.824	−0.593	−0.426	−0.103
TS	−0.366	−0.466	0.889	−0.477	−0.106	−0.835
Products	−0.637	−0.583	0.832	−0.560	−0.108	−0.113

Table 4a. Bond order evolution and synchronicity parameter for methyl 3-chloropropionate gas-phase elimination

	C_6—Cl_{13}	C_6—C_5	C_5—H_{14}	H_{14}—Cl_{13}
Reactant	1.0018	1.0182	0.8875	0.0024
TS	0.3958	1.3465	0.4327	0.3476
Products	0.0066	1.9100	0.0122	0.9000
δB_i	0.609	0.368	0.520	0.385
% Ev	60.9	36.8	52.0	38.5
δB_{av}		0.47		
Sy		0.87		

Table 4b. Bond order evolution and synchronicity parameter for methyl 4-chlorobutyrate gas-phase elimination

	C_7—O_6	O_6—C_4	C_4—O_5	O_5—C_3	Cl_8—C_3	Cl_8—C_7
Reactant	0.878	1.038	1.750	0.001	0.993	0.000
TS	0.682	1.395	1.193	0.833	0.001	0.138
Products	0.006	1.790	1.010	0.879	0.000	1.008
δB_i	0.225	0.474	0.752	0.947	0.999	0.136
% Ev	22.51	47.38	75.22	94.73	99.92	13.65
δB_{av}		0.59				
Sy		0.68				

Table 4c. Bond order evolution and synchronicity parameter for methyl 5-chlorovalerate gas-phase elimination

	C_8—O_7	O_7—C_1	C_1—O_6	O_6—C_5	C_5—Cl_9	Cl_9—C_8
Reactant	0.875	1.022	1.766	0.000	0.991	0.000
TS	0.688	1.367	1.214	0.817	0.000	0.132
Products	0.006	1.766	1.015	0.867	0.000	1.007
δBi	0.22	0.46	0.74	0.94	1.00	0.13
% Ev	21.52	46.41	73.51	94.30	99.97	13.11
δBav			0.58			
Sy			0.68			

The Synchronicity parameters Sy = 0.87 for methyl chloroprionate, 0.68 for both methyl chlrobutyrate and methyl chlorovalerate suggest a polar concerted mechanism, thus implying TS with ion-pair character for lactone forming substrates.

CONCLUSIONS

The gas-phase elimination of hydrogen chloride from methyl 3-chloropropionate, and lactone formation from methyl 4-chlorobutyrate and methyl 5-chlorovalerate has been investigated to provide explanation to the experimental products observed. For methyl 3-chloropropionate dehydrochlorination is the sole reaction observed. In the case of methyl 4-chlorobutyrate and methyl 5-chlorovalerate, the dehydrochlorination and lactone formation show similar barriers implying that both reactions occur in parallel-competitive fashion. Hydrogen chloride elimination to give the corresponding olefin, proceeds through polar four-member transition state, with a symmetrical IRC profile. The four atoms participating in the reaction are in an almost planar configuration. The parallel reaction producing methyl chloride and lactone intermediate from methyl 4-chlorobutyrate and methyl 5-chlorovalerate takes place through late TS resembling the lactone; thus forming a five- or six-membered ring configuration, respectively. Reasonable agreement with the experimental parameters was found at B3LYP/6-31G* level of theory. The presence of the ester moiety suggests neighboring group participation by the carbonyl oxygen in the parallel lactone-forming reaction. Structural parameters, partial charges, and NBO analysis suggest that bond polarization of Cl—C bond is the determining factor in both elimination reactions, being most advanced in lactone forming compounds where the TS is best described as an intimate ion-pair. The synchronicity parameter also reflects the nature of the TS. For more advanced TS found for methyl 4-chlorobutyrate

and methyl 5-chlorovalerate the synchronicity parameter Sy = 0.68. This value implies a more asynchronic mechanism when compared to hydrogen chloride elimination from methyl 3-chloropropionate with Sy = 0.87.

REFERENCES

[1] A. Maccoll, *Chem. Rev.* **1969**, *69*, 33–60.
[2] G. G. Smith, F. W. Kelly, *Prog. React. Kinet.* **1971**, *8*, 75–234.
[3] W. H. Saunders, Jr, A. F. Cockerill, *Mechanism of Elimination Reactions*, Chapter VIII, Wiley-Interscience, New York, **1973**, 378.
[4] K. W. Egger, A. T. Cocks, *Chemistry of Carbon-Halogen Bond*, (Ed.: S. Patai), Chapter 10, Wiley, Chichester, **1973**, 703.
[5] G. Chuchani, *The Chemistry of Halides, Pseudo-Halides and Azides*, (Ed.: S., Patai, Z. Rapopport), Chapter 19, Wiley, New York, **1995**, 1069.
[6] A. Maccoll, P. J. Thomas, *Nature.* **1955**, *176*, 392–393.
[7] S. W. Benson, A. H. Bose, *J. Chem. Phys.* **1963**, *39*, 3463–3473.
[8] H. E. O'Neal, S. W. Benson, *J. Phys. Chem.* **1967**, *71*, 2903–2921.
[9] A. Maccoll, P. J. Thomas, *Prog. React. Kinet.* **1967**, *4*, 119–148.
[10] A. Maccoll, E. S. Swinbourne, *J. Chem. Phys.* **1964**, 149–153.
[11] J. S. Shapiro, E. S. Swinbourne, *Can. J. Chem.* **1968**, *46*, 1341–1349.
[12] R. C. L. Bricknell, A. Maccoll, *Chem. Ind. (London).* **1961**, 1912–1913.
[13] H. Martin, R. Hoffman, A. Maccoll, *J. Am. Chem. Soc.* **1965**, *87*, 3774–3775.
[14] H. Kwart, M. T. Waroblak, *J. Am. Chem. Soc.* **1967**, *89*, 7145–7146.
[15] G. Chuchani, A. Rotinov, R. M. Dominguez, *Int. J. Chem. Kinet.* **1982**, *14*, 381–397.
[16] G. Chuchani, R. M. Dominguez, A. Rotinov, *Int. J. Chem. Kinet.* **1987**, *19*, 781–785.
[17] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gnzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, ES Replogle, JA Pople, Gaussian 98, Revision A.3,Gaussian, Inc., Pittsburgh, PA, **1998**.
[18] D. McQuarrie, *Statistical Mechanics*, Harper & Row, New York, **1986**.
[19] J. B. Foresman, Æ. Frish, *Exploring Chemistry with Electronic Methods* (2nd edn), Gaussian, Inc, Pittsburg, PA, **1996**.
[20] S. W. Benson, *The Foundations of Chemical Kinetics*, Mc-Graw-Hill, New York, **1960**.
[21] H. E. O'Neal, S. W. Benson, *J. Phys. Chem.* **1967**, *71*, 2903–2921.
[22] S. W. Benson, *Thermochemical Kinetics*. John Wiley & Sons, New York, **1968**.
[23] G. J. Lendvay, *J. Phys. Chem.* **1989**, *93*, 4422–4429.
[24] A. E. Reed, R. B. Weinstock, F. Weinhold, *J. Chem. Phys.* **1985**, *83*(2), 735–746.
[25] A. E. Reed, L. A. Curtiss, F. Weinhold, *Chem. Rev.* **1988**, *88*, 899–926.
[26] K. B. Wiberg, *Tetrahedron* **1968**, *24*, 1083–1095.
[27] E. D. Glende, A. Moyano, M. A. Periclas, E. Valenti, *J. Org. Chem.* **1989**, *54*, 573–582.
[28] A. Moyano, M. A. Periclas, E. Valenti, *J. Org. Chem.* **1989**, *54*, 573–582.

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