



Theoretical calculations on the gas-phase thermal decomposition kinetics of selected thiomethyl chloroalkanes: A new insight of the mechanism



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ARTICLE INFO

Article history:

Received 23 October 2013

Accepted 8 November 2013

Available online 16 November 2013

Keywords:

2-Thiomethyl-1-chloroethane

4-Thiomethyl-1-chlorobutane

Kinetics

Thermal decomposition

Theoretical calculations

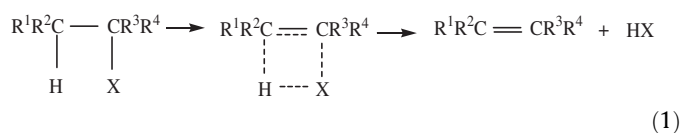
ABSTRACT

Theoretical calculations of the gas-phase thermal decomposition kinetics of 2-thiomethyl-1-chloroethane and 4-thiomethyl-1-chlorobutane have been carried out by using Density Functional Theory (DFT), composite CBS-Q3, and Møller-Plesset second-order (MP2) methods in order to elucidate a reasonable reaction mechanism of these compounds. The enhanced reactivities of these two substrates, when compared with their parent compounds, attributed to neighboring group participation (NGP) or anchimeric assistance in the literature, were investigated. For 2-thiomethyl-1-chloroethane two dehydrochlorination pathways, with and without NGP were studied. The results of quantum chemical estimations of 2-thiomethyl-1-chloroethane in the gas phase show good agreement with experimental values at B3LYP/6-31++G(2d,p) level, and suggest the 1,2-elimination through non-synchronous four-membered cyclic transition state is the preferred mechanism. For 4-thiomethyl-1-chlorobutane, the significant increase in rate compared to 2-thiomethyl-1-chloroethane, together with the formation of a cyclic product tetrahydrothiophene suggest the anchimeric assistance by the CH₂S group in the transition state. Best calculated parameters were obtained with CAM-B3LYP/6-31G++(2d,p). Results support the NGP of the thiomethyl group, through cyclic ion-pair type of intermediate. The bond polarization of the C–Cl, in the direction of C^{δ+}...Cl^{δ-}, appears to be the rate determining step of these decompositions.

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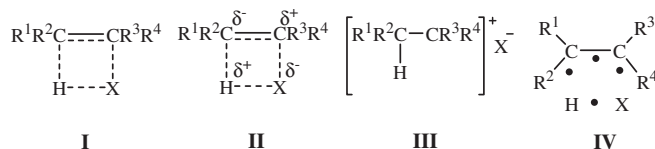
1. Introduction

The gas-phase pyrolysis or elimination of simple alkyl halides are well known to decompose into the corresponding olefin and hydrogen halide, reaction (1) [1–5].



The most accepted mechanism is a four-membered cyclic transition state (I), where a β-hydrogen adjacent to the C–X is necessary for molecular decomposition in reaction (1) [1–5]. An additional proposed mechanism consists in the polarization of the C–X bond (C^{δ+}...X^{δ-}), with the participation of the adjacent C–H bond (II) [6]. Moreover, a very polar nature of this reaction in terms of

an intimate ion-pair intermediate was also considered (III) [7], while the semi-ion pair transition state structure (IV) was postulated by Benson et al. [8].



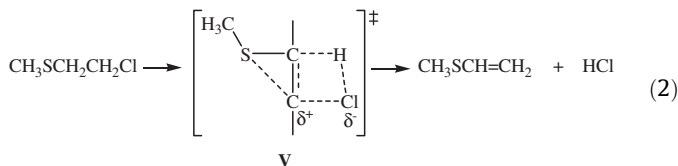
The proposed mechanism of the intimate ion-pair intermediate (III) led to several investigations to examine the feasibility of rearrangements and neighboring group participation in gas-phase reactions under homogeneous experimental conditions. These types of phenomena are well known to take place with ionic or charged intermediates present in solutions. However, to conceive these species in homogeneous gas-phase reaction is very difficult. This thought derives from the fact that there are no driving forces, such as solvent, catalyst, and reagents, present to stabilize possible ionic or charged species during the process under homogeneous

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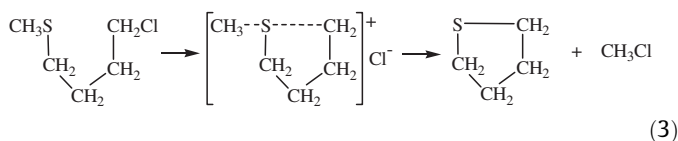
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decomposition in the gas phase. Otherwise, if intermediate (III) occurs in the gas phase, then, it is possible that some internal rearrangements and neighboring group participation mechanisms may take place. Works related to these types of mechanisms in gas-phase of elimination or thermal decomposition kinetics of halogen compounds, under homogeneous conditions, have been described and reported [5].

Apparently, the first convincing example of neighboring group participation in homogeneous gas-phase reaction reported in the literature was believed to be in the elimination kinetics of 2-thiomethyl-1-chloroethane, reaction (2) [9]. This compound was found to be 234 times faster than the corresponding parent compound 1-chloroethane.



The greatly enhanced rate of the sulfur compound was explained due to the anchimeric assistance of the sulfur atom [V]. Cyclization rates for the anchimeric assistance of a substituent in neighboring group participation occur in the order $5 > 6 > 3$ [10]. A further work in the gas-phase elimination kinetics of 4-thiomethyl-1-chlorobutane, where tetrahydrothiophene and methyl chloride were produced, reaction (3) [11], showed a considerable higher elimination rate, 720 times faster with respect to the unsubstituted chloride, 1-chlorobutane.



This result suggested the CH_3S group provided anchimeric assistance through a five-membered conformation. The formation of the cyclic product tetrahydrothiophene was explained as unequivocal neighboring group participation through an intimate ion-pair mechanism.

In association with the previous-mentioned work, the gas-phase elimination kinetics of selected methoxyalkyl chlorides [12] were undertaken, where the CH_3O group in 4-methoxy-1-chlorobutane was believed to assist anchimerically the process of elimination. This interpretation was derived by the formation of tetrahydrofuran, in addition to the normal dehydrohalogenated product. Moreover, the significantly higher relative rate of elimination for 4-methoxy-1-chlorobutane when compared to the parent compound ethyl chloride was thought to be due to the participation of the neighboring CH_3O substituent, through five-membered ring conformation. The mechanism was explained in terms of an intimate ion-pair by intramolecular solvation or autosolvation of the chloride ion.

Recently, Density Functional Theory (DFT) calculations were carried out in order to explain a reasonable mechanism of decomposition of the above-mentioned compound [13]. Calculation results suggested that in addition of the 1,2-elimination mechanism, the anchimeric assistance of the CH_3O group, through a polar five-centered cyclic transition state, provided an additional pathways to give tetrahydrofuran and chloromethane. The bond polarization of the C–Cl, in the direction of $\text{C}^{\delta+} \cdots \text{Cl}^{\delta-}$, was thought to be rate determining of these elimination reactions. The significant increase in rate together with the formation of a cyclic product tetrahydrofuran in the gas-phase thermal decomposition of 4-methoxy-1-chlorobutane was attributed to neighboring group participation (NGP) by the CH_3O oxygen atom in the transition state. Calculated

thermodynamic and kinetic parameters were found in reasonable agreement with the reported experimental results.

Considerations of the faster rate of 2-thiomethyl-1-chloroethane with respect to the parent compound 1-chloroethane, plus the unusual formation of an approximate quantitative yield (96%) of the cyclic product tetrahydrothiophene from 4-thiomethyl-1-chlorobutane, compared to $\approx 40\%$ of tetrahydrofuran from 4-methoxy-1-chlorobutane, motivated the present quantum chemical calculations study to propose a reasonable mechanism of decomposition of 2-thiomethyl-1-chloroethane and 4-thiomethyl-1-chlorobutane, and determine the possible neighboring group participation (NGP) of the thiomethyl group in both of these substrates. In this sense, the potential energy surfaces (PESs) were examined by using the DFT, composite CBS-Q3, and MP2 level of theories and the results analyzed and compared to the experimental data.

Experimental kinetic data of an elementary step does not necessarily leads to a reasonable interpretation of a reaction mechanism. However, interaction between theory and experiments may be more profitable in the elucidation of thermal decomposition processes of organic molecules in the gas phase.

2. Computational methods and models

The elimination kinetics and mechanisms of 2-thiomethyl-1-chloroethane and 4-thiomethyl-1-chlorobutane in the gas phase were studied by density functional methods B3LYP, CAM-B3LYP, MPW1PW91, and perturbation method MP2, with 6-31G++(2d), 6-31G++(2d,p) basis sets, and the composite method CBS-QB3, implemented in Gaussian 09 [14]. The Transition States (TS) search was carried out by using Quadratic Synchronous Transit QST protocol. The nature of stationary points was determined by means of normal-mode analysis. The unique imaginary frequency in the transition states (TS) associated with the transition vector (TV), i.e., the eigenvector associated with the unique negative eigenvalue of the force constant matrix was characterized.

For geometry optimizations, the Bery analytical gradient optimization routines were used, with convergence on the density matrix was 10^{-9} atomic units, threshold value for maximum displacement 0.0018 Å, and maximum force was 0.00045 Hartree/Bohr.

The thermodynamic values of zero-point vibrational energy (ZPVE), temperature corrections ($E(T)$) and absolute entropies ($S(T)$), were obtained from frequency calculations. Temperature corrections and absolute entropies were obtained when considering ideal gas behavior from the harmonic frequencies and moments of inertia by standard methods [15] at average temperature and pressure values within the experimental range. Scaling factors for frequencies and zero point energies were cited from the literature [16,17].

The first order rate coefficient k was calculated using the transition state theory TST assuming that the transmission coefficient is equal to 1 as expressed in the following equation (1):

$$k = (k_B T/h) \exp(-\Delta G^\ddagger/RT) \quad (1)$$

where ΔG^\ddagger is the Gibbs free energy change between the reactant and the transition state, k_B , h are the Boltzmann and Planck constants respectively. ΔG^\ddagger was calculated using the following relations [Eqs. (2) and (3)]:

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \quad (2)$$

$$\text{and } \Delta H^\ddagger = V^\ddagger + \Delta ZPVE + \Delta E(T) \quad (3)$$

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