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Research paper

Kinetics and mechanism of the reactions of chloromethyl radical with acetylene and decomposition of 1-chloroallyl and 2-chloromethyl vinyl radicals

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ABSTRACT

Three reactions occurring on the C_3H_4Cl potential energy surface (PES) were studied computationally using quantum chemistry and master equation/RRKM: $CH_2Cl + C_2H_2 \rightarrow$ Products (1), $CH_2CHCHCl \rightarrow$ Products (2), and $CH_2ClCHCH \rightarrow$ Products (3). The results indicate low importance of the 1,3-Cl shift channel linking the PESs of reactions 1 and 2 despite a relatively low energy barrier. Addition and chemically activated H elimination are the two major products of reaction 1, with branching dependent on pressure and temperature. Cl and cyclopropene are the major products of reaction 2, and $CH_2Cl + C_2H_2$ – of reaction 3.

1. Introduction

Kinetic modeling of such processes as oxidation, pyrolysis, and incineration of chlorinated hydrocarbons, as well as chlorination of hydrocarbons, is critical for successful use of their respective chemical mechanisms for prediction and control. The success of such kinetic modeling is limited by a lack of fundamental information on the rates and products of many elementary reactions involving chlorinated hydrocarbon species (e.g., [1–4]). Use of kinetic parameters derived from analogies with non-chlorinated hydrocarbons is widespread; however, such an approach must be used with caution because the presence of chlorine atoms frequently results in different patterns of reactivity and/or dramatic differences between the actual rate constants and those expected from analogy (e.g., [5,6]). One example of deviation from hydrocarbon-like behavior is the propensity of the chlorine atom to undergo isomerization shifts between carbon atoms where similar H-atom require prohibitively large energy barriers (e.g., [3,7–9]).

In the current work, mechanisms and kinetics of two reactions occurring on the same potential energy surface (PES) were investigated:

$$CH_2Cl + C_2H_2 \rightarrow \text{Products} \quad (1)$$

and

$$CH_2CHCHCl \rightarrow \text{Products} \quad (2)$$

Addition of the chloromethyl radical to the triple bond of acetylene can be expected to play a role similar to that of the reaction between the methyl radical and acetylene in hydrocarbon pyrolysis and combustion, i.e., leading to the formation of propyne (CH_3-CCH), thus contributing to the generation of propargyl radicals and nucleation of aromatics (e.g., [10–12]). Chlorinated methyl radicals have greater kinetic stability in the combustion environment than their non-chlorinated analog due to the weaker C—O bonds in the peroxy adducts formed by the addition to the O_2 molecule ([13] and references therein). Therefore, they can be expected to accumulate in high concentrations in flames.

In the $CH_3 + C_2H_2$ reaction, the main two channels are the formation of the stabilized CH_3CHCH adduct and the chemically activated elimination of the hydrogen atom leading to the formation of propyne [10–12]; isomerization of the adduct to the more thermodynamically stable allyl (CH_2CHCH_2) form has a prohibitively large barrier. In the case of the chlorinated methyl, a possibility opens for the initial $CH_2Cl{-}CH{=}CH$ adduct to isomerize via a 1,3 Cl shift, thus forming the more stable 1-chloroallyl radical, which, if formed, can further contribute to the molecular mass and aromatics growth in a way similar to that observed in the non-chlorinated hydrocarbon pyrolysis and combustion systems (e.g., [2,14]).

1-Chloroallyl radical can also form in a variety of other reactive pathways, including those analogous to the reactions forming the allyl radical in non-chlorinated systems. Thermal decomposition

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of the 2-chloroallyl radical has been studied both experimentally and computationally [15]; however, nothing is known about the mechanism and kinetics of the thermal reaction of the more stable 1-chloroallyl radical. Because of the possible isomerization between $CH_2Cl—CH═CH$ and 1-chloroallyl, the PES of reactions 1 and 2 are linked; the resultant combined PES was studied in the current work and the mechanisms and kinetics of these reactions were investigated. The kinetics of the thermal decomposition of the $CH_2Cl—CH═CH$ radical was also studied.

2. Potential energy surface (PES)

Molecular structures were optimized and vibrational frequencies were calculated for all PES stationary points using the CCSD method with the 6-31 + G(d,p) basis set [16]. The CCSD(T) method [17,18] was used for single-point energy calculations for all stationary points. The aug-cc-pVDZ, aug-cc-pVTZ, and aug-cc-pVQZ basis sets were used [19]; complete basis set (CBS) extrapolation was performed using the method of [20]. The Gaussian 09 program [21] was employed in all potential energy surface calculations.

The PES of reactions 1 and 2 is displayed in Fig. 1; to assist in its interpretation, the individual transformations that can occur on the PES are shown in Chart 1. All reactant and product sets, as well as intermediates, are numbered to facilitate data handling and discussion, as indicated in Fig. 1 and Chart 1. Addition of the CH_2Cl radical to C_2H_2 results in the formation of the chemically activated $CH_2Cl—CH═CH$ radical (3). This adduct can decompose back to the reactants (5), to H + CH_2ClCCH (7), stabilize via collisions with the bath gas, or isomerize via a Cl atom 1,3-transfer to a delocalized *cis*-$CH_2CHCHCl$ 1-chloroallyl radical (1). Decomposition to H + CH_2ClCCH energy barrier is 33.7 kJ mol^{-1} higher than that of the entrance addition reaction; the barrier to isomerization is lower than that of decomposition of $CH_2Cl—CH═CH$, at 22.4 kJ mol^{-1} - above the addition barrier. These barrier values indicate that the main process for the $CH^2Cl—CH═CH$ adduct is likely to be the reverse decomposition at low pressures and collisional stabilization at high pressures. The importance of the other two processes should increase with temperature, as the energy distribution of the adduct resulting from chemically activation spreads to higher energies.

The chemically activated *cis*-1-chloroallyl radical (1) can easily and reversibly isomerize to its *trans* form (2) by overcoming a low 61.6 kJ mol^{-1} barrier. The energies of the *cis* and the *trans* forms of the 1-chloroallyl radical differ by only 2.7 kJ mol^{-1}. Only the *cis* form (1) can isomerize back to $CH_2Cl—CH═CH$ (3). Both isomers of 1-chloroallyl can decompose by H atom elimination to form the H + CH_2CCHCl (6) product. These decomposition processes proceed through the same transition state (PES saddle point) structure: H atom departure is preceded by a rotation of the —CHCl group relative to the vinyl group of 1-chloroallyl, from the planar configuration where all atoms are in the same plane to that with the plane formed by the three atoms of the —CHCl group perpendicular to the plane of all other atoms, including the departing hydrogen atom. An image of this transition state structure is presented in Table 1S in the Supporting material. Another possible transformation process of both isomers of the 1-chloroallyl radical (1 and 2) is closing of the ring to form the 2-chloro-cyclopropyl radical (4), with energy barriers of 209.2 and 216.7 kJ mol^{-1}, respectively. The *cyc*-$CH_2CHCHCl$ (4) product of ring closure is rather unstable relative to 1-chloroallyl, with the barriers of only 76.6 and 86.8 kJ mol^{-1} for reverse ring opening. However, it serves as an intermediate for a chlorine atom departure reactive pathway leading to the cyclopropene + Cl products (8), with the overall energy threshold that is similar to that of the H elimination from 1-chloroallyl, 3.2 kJ mol^{-1} lower than the latter.

The PES of the 2-chloro-cyclopropyl radical (4) decomposition to cyclopropene + Cl (8) is illustrated in Fig. 2. Here, relaxed PES scans were performed in the system of coordinates illustrated in the inset in Fig. 2. The scanned coordinates were the X–Cl distance and the C–X–Cl angle, where X is the point equidistant from the two carbon atoms of the forming double bond of the cyclopropene product. The minimum energy path proceeds from one of the two identical *cyc*–$CH_2CHCHCl$ PES wells through formation of a symmetric bridged structure with Cl equidistant from the two carbon atoms and then Cl atom departure via increasing X–Cl distance. The second stage of the process occurs on a shallow part of the PES and is likely characterized by a 'loose' [22] transition state. The C–X–Cl angle scan performed with the X–Cl coordinate relaxed indicates a very shallow PES minimum (the lower part of Fig. 2) with the depth of only a small fraction of a kJ mol^{-1}, which cannot contain any bound vibrational states and therefore is not an intermediate in the dissociation process. The qualitative shape of the PES is very similar to those found for other reactions of beta-scission of chlorinated hydrocarbon radicals via Cl elimination and simultaneous formation of a π bond [15,23,24].

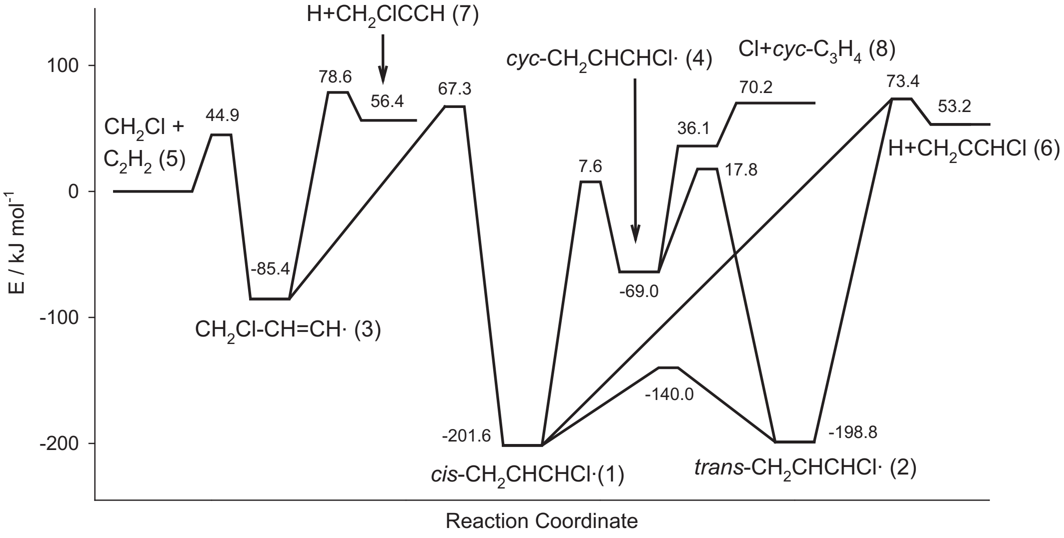

Fig. 1. Potential energy surface of reactions 1 and 2.