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Density Functional Theory Study of the Mechanisms of Oxidation of Ethylene by Chromyl Chloride

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The mechanistic pathways for the formation of epoxide, 1,2-dichloroethane, 1,2-chlorohydrin, acetaldehyde, and vinyl alcohol precursors in the oxidation of ethylene by chromyl chloride has been studied using hybrid density functional theory at the B3LYP/LACVP* level of theory. The formation of the epoxide precursor ($Cl_2(O)Cr\text{-}OC_2H_4$) was found to take place via initial [2 + 2] addition of ethylene across the Cr═O bonds of CrO_2Cl_2 to form a chromaoxetane intermediate. The pathway involving initial [3 + 2] addition of ethylene to the oxygen and chlorine atoms of CrO_2Cl_2, which has not been explored in earlier studies, was found to be favored over [3 + 2] addition of olefin to two oxygen atoms of CrO_2Cl_2. The formation of the 1,2-dichloroethane precursor, which was found to take place via [3 + 2] addition of ethylene to two chlorine atoms of CrO_2Cl_2, is slightly favored over the formation of the epoxide precursor. The 1,2-chlorohydrin precursor has been found to originate from [3 + 2] addition of ethylene to the oxygen and chlorine atoms of CrO_2Cl_2 as opposed to [2 + 2] addition of ethylene to the Cr−Cl bond. The vinyl alcohol precursor $O{=}CrCl_2{-}(OH)CH{=}CH_2$ has been found to exist only on the triplet potential energy surface. The acetaldehyde precursor ($O{=}CrCl_2{-}OCHCH_3$) was found to be the most stable species on the reaction surface. Hydrolysis may be required to generate the epoxide, 1,2-dichloroethane and 1,2-chlorohydrin from the respective precursors.

Introduction

The oxidation of alkenes by transition metal oxo species such as OsO_4, RuO_4, MnO_4^-, and Cr(VI) oxo complexes is of central importance in preparative organic chemistry. Oxidation carried out in this way is often relatively gentle and remarkably specific compared to the direct application of elemental oxygen.[1]

A number of mechanistic questions surrounding the reaction of transition metal oxo complexes with alkenes remain unresolved, despite having been the subject of extensive experimental and theoretical studies.[2−9] Mechanistic proposals put forward in the past to explain the interaction of transition metal oxo units with C−C π bonds have often been untested by experiment and based on limited precedent. An understanding of the mechanism of oxidation of alkenes by Cr(VI) oxo species has been hindered by the fact that diverse solvents and ligands have been utilized in the various experimental studies reported, and these factors can have dramatic effects on the course of the reaction.[10]

A well-known example of the mechanistic dilemma of olefin oxidation is the bishydroxylation of alkenes by OsO_4, $KMnO_4$, and related species. Criege et al.[11,12] proposed a concerted [3 + 2] cycloaddition pathway (path A in Scheme 1). This proposal won wide acceptance among organic chemists,[13−15] in part because of the ease with which analogy can be drawn with other dipolar cycloadditions. Theoretical work also suggested that such a hypothesis is consistent with calculations on species presumably lying on the reaction coordinate.[16,17] The formal product of the [3 + 2] addition, a five-membered metallacycle (osma-2,5-dioxolane), was experimentally characterized, which upon hydrolysis give diols.[15]

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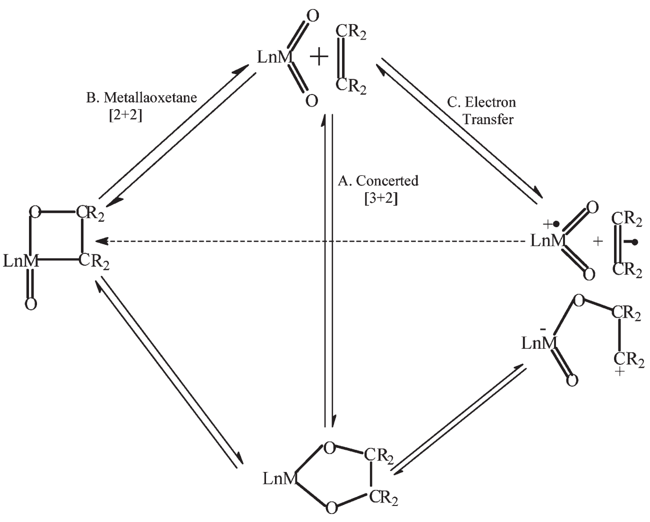
Scheme 1. Possible Pathways for the Reaction of $LnMO_2$ with Alkene[18]



Unlike OsO_4 and $KMnO_4$ which react with olefins to form predominantly diols without significant epoxide formation, chromyl chloride reacts with alkenes to form predominantly epoxides, without diol formation[15] as might be expected from path A of Scheme 1. The concerted [3 + 2] pathway was thus challenged by Sharpless and co-workers,[2,19−21] who asserted that all known data could easily be explained by a stepwise mechanism involving [2 + 2] cyclization to form a metallaoxetane (path B of Scheme 1). The underlying assumption of this mechanism is that the olefin, albeit a weak nucleophile, always interacts initially with the metal center, followed by formation of a d^0 organometallic intermediate. The intermediate subsequently rearranges to the five-membered metallacycle.

Kochi et al.[22,23] have also proposed a third mechanism (path C in Scheme 1), to explain the oxidation of olefins by oxo transition metal complexes. It involves an initial electron transfer, and addition of the odd electron intermediate to give a metallaoxetane and/or metalladiolate.

In Scheme 2, the two reaction pathways (A and B), which were suggested to arise from the π- complex **2**, lead to the formation of the Cr(IV) organometallic intermediates. In path A, there is alkene insertion into the Cr−Cl bond (cis-chlorometalation) to give the alkylchromium intermediate **3**. The dichloride **5** and the chromium derivative of the chlorohydrin **6** are subsequently generated from **3** by reductive elimination (path a) and by migration of the alkyl group from the chromium to the oxygen (path a'), respectively. The four-membered ring intermediate **4**, formed via [2 + 2] cycloaddition from the π-complex **2** in path B, leads to the formation of either the chlorohydrin precursor **6**(path b) or the epoxide precursor **7** (path b′). Sharpless et al.[2] reasoned that the formation of the organometallic intermediates in Scheme 2 could rationalize the primary products of epoxides, chlorohydrins, and dichlorides formed from cis-addition of ethylene to chromyl chloride (Scheme 3).

Evidence for the stepwise mechanism was provided by nonlinear Eyring plots of enantioselectivity as a function of the reciprocal of temperature for asymmetric dihydroxylations.[24] Support for the [2 + 2] addition in the oxidation of olefins by chromyl chloride was provided by Goddard et al. [5,6,9] in a theoretical work on olefin oxidations.

Frenking et al.,[25] Morokuma et al.,[26] and Ziegler et al.[27] computed the [2 + 2] and [3 + 2] activation barriers for the reaction of OsO_4 with ethylene and found out that the activation energy of the [2 + 2] addition to form the four-membered cyclic metallaoxetane was very high (>39 kcal mol^{-1}) whereas the activation energy for the [3 + 2] addition to form the five-membered metallacycle(osma-2,5-dioxolane) was much smaller (<10 kcal mol^{-1}), indicating that the addition reaction follows the concerted [3 + 2] mechanism. Houk et al.[28] also compared computed and measured kinetic isotope effects and corroborated the concerted reaction pathway for the addition reaction of OsO_4 with ethylene. Ziegler et al.[29] also carried out density functional theory (DFT) calculations on the [2 + 2] and [3 + 2] addition of ethylene to Cr=O bonds in CrO_2Cl_2 and found the [3 + 2] addition to form the five-membered metallacycle to be more favorable than the [2 + 2] addition to form the four-membered cyclic chromaoxetane. In another study, Ziegler et al.[30] found out that contrary to earlier assumptions,[2] the formation of the epoxide precursor from the reaction between CrO_2Cl_2 and ethylene does not involve a chromaoxetane intermediate derived from [2 + 2] cycloaddition to the Cr=O linkage but rather an ester intermediate derived from [3 + 2] addition of ethylene to the chromium−oxygen bonds in CrO_2Cl_2. They also concluded that the chlorohydrins should arise from a [3 + 2] cycloaddition. In matrix isolation experiments, Limberg et al.[31,32] have produced IR-spectroscopic proof for $O{=}CrCl_2$-epoxide and $O{=}CrCl_2$-acetaldehyde complexes as primary products in olefin oxidation with chromyl chloride (CrO_2Cl_2).

In this work, the reactions between CrO_2Cl_2 and ethylene leading ultimately to the formation of ethylene oxide (epoxide), 1,2-chlorohydrin, 1,2-dichloroethane, vinyl alcohol, and acetaldehyde (Schemes 4 and 5) are studied theoretically using hybrid DFT. The geometries and relative energies of the reactants, transition states, relevant intermediates, and products are computed to help provide insight into the mechanistic channel of these reactions.

Calculation Procedure

All calculations were carried out with the SPARTAN '06 V112 Molecular Modeling program[33] at the DFT B3LYP/

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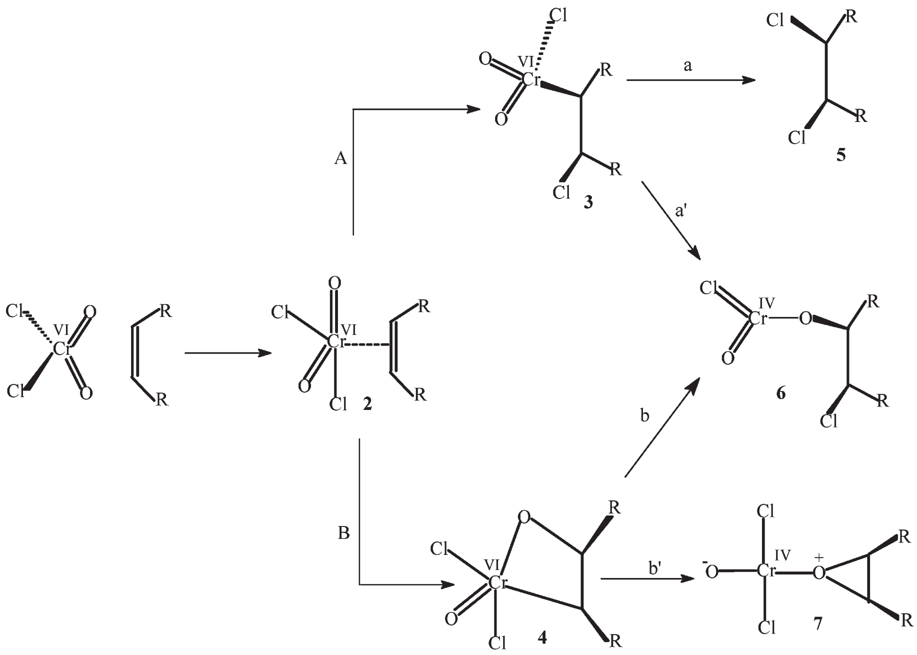
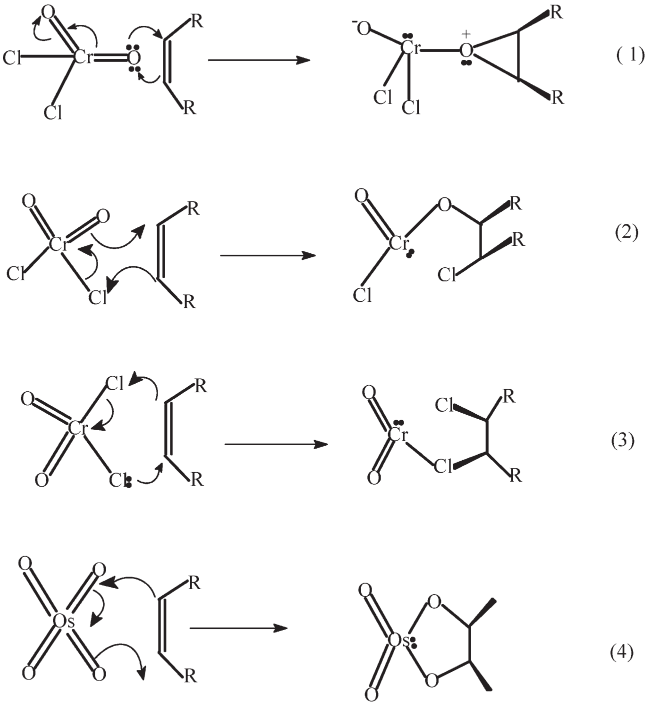
Scheme 2. Proposed Mechanism for Reaction of Cl_2CrO_2 with Ethylene Involving Organometallic Intermediates[2]



Scheme 3. Mechanism Involving Direct Attack on the Heteroatom Ligands[2]



LACVP* level of theory. The LACVP* basis set is a relativistic effective core-potential that describes the atoms H−Ar with the 6-31G* basis while heavier atoms are modeled with the LANL2DZ basis set which uses the all-electron valence double-ζ basis set (D95 V), developed by Dunning, for first row elements[34] and the Los Alamos ECP plus double-ζ basis set developed by Wadt and Hay for the atoms Na−La, Hf−Bi.[35−37]

The starting geometries of the molecular systems were constructed using SPARTAN's graphical model builder and minimized interactively using the sybyl force field.[38] All geometries were fully optimized without any symmetry constraints. The optimized geometries were subjected to full frequency calculations to verify the nature of the stationary points. Equilibrium geometries were characterized by the absence of imaginary frequencies. The transition state structures were located by a series of constrained geometry optimizations in which the forming- and breaking-bonds were fixed at various lengths while the remaining internal coordinates were optimized. The approximate stationary points located from such a procedure were then fully optimized using the standard transition state optimization procedure in SPARTAN. All first-order saddle-points were shown to have a Hessian matrix with a single negative eigenvalue, characterized by an imaginary vibrational frequency along the reaction coordinate. All the computations were performed on Dell Precision T3400 Workstation computers.

Results and Discussion

The DFT geometry optimization of the Cl_2CrO_2 reactant gave a structure (singlet) **A1** (Scheme 4 and Figure 1) with C_{2v} symmetry, in agreement with experiment.[39] The two Cr=O double bonds are each 1.555 Å long and 108.55° apart. These values are in good agreement with the experimentally estimated values of 1.581 Å and 108.5°[39] and the calculated values of 1.571 Å and 108.7° respectively.[29] The two Cr−Cl bonds are each 2.114 Å long and 111.27° apart. These values are also in good agreement with the experimentally determined values of 2.126 Å and 113.3° respectively[39] and the calculated values of 2.104 Å and 112.0° respectively.[29] A triplet **A1** (**A1/t**) has been computed to be 38.03 kcal mol^{-1} less stable than the singlet **A1**.

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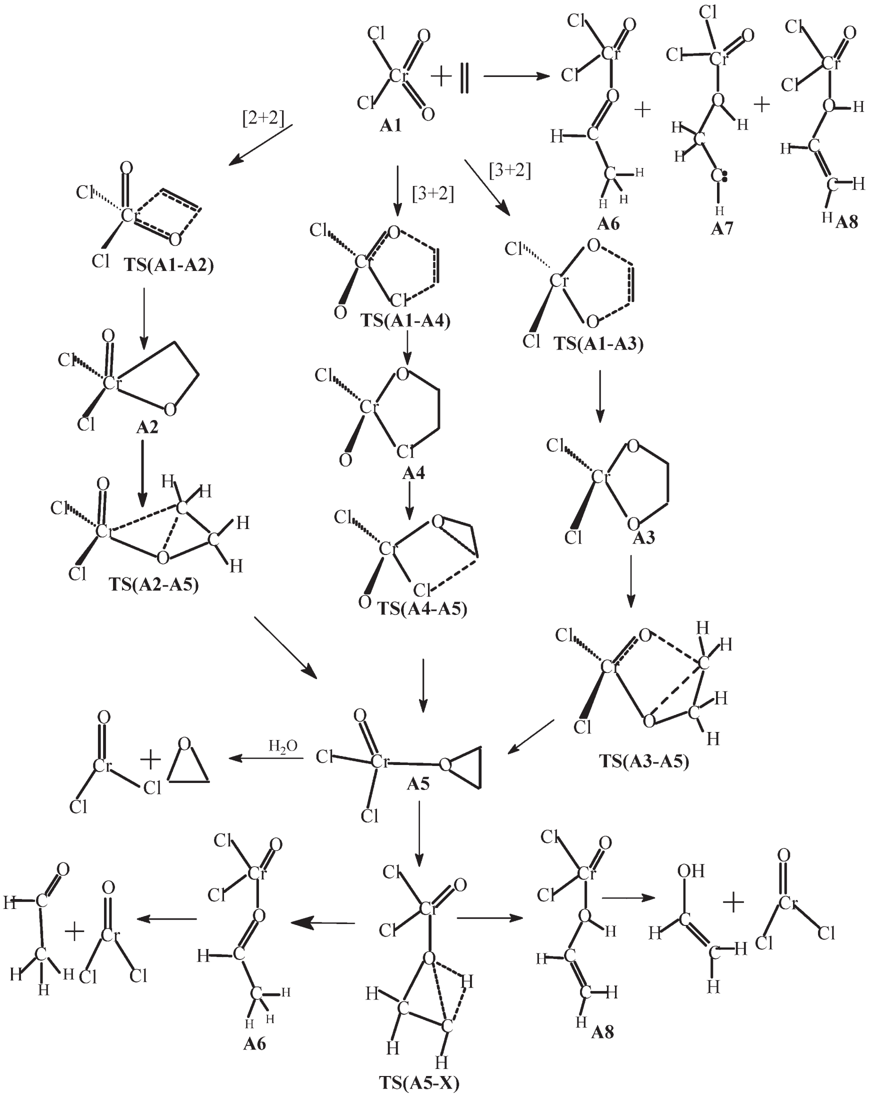
Scheme 4. Mechanisms of the CrO_2Cl_2-Mediated Formation of Epoxide, Acetaldehyde, and Vinyl Alcohol



The interaction of the Cl_2CrO_2 and ethylene apparently does not lead to a π-bonded complex. An extensive search of the singlet and triplet potential energy surface (PES) in an attempt to locate a π-bonded complex proved unsuccessful.

1. Formation of Epoxide. In most mechanistic studies, the species **A5** (Scheme 4 and Figure 1) has been invoked as the direct precursor for epoxide. This species was postulated by Sharpless et al.[2] as the immediate precursor of epoxide and by Limberg et al. [31] as the oxirane adduct intermediate leading to acetaldehyde. Limberg and Köppe[32] isolated the propylene analogue of **A5** in the reaction between CrO_2Cl_2 and propylene.

Species **A5** could in principle arise from four separate pathways:

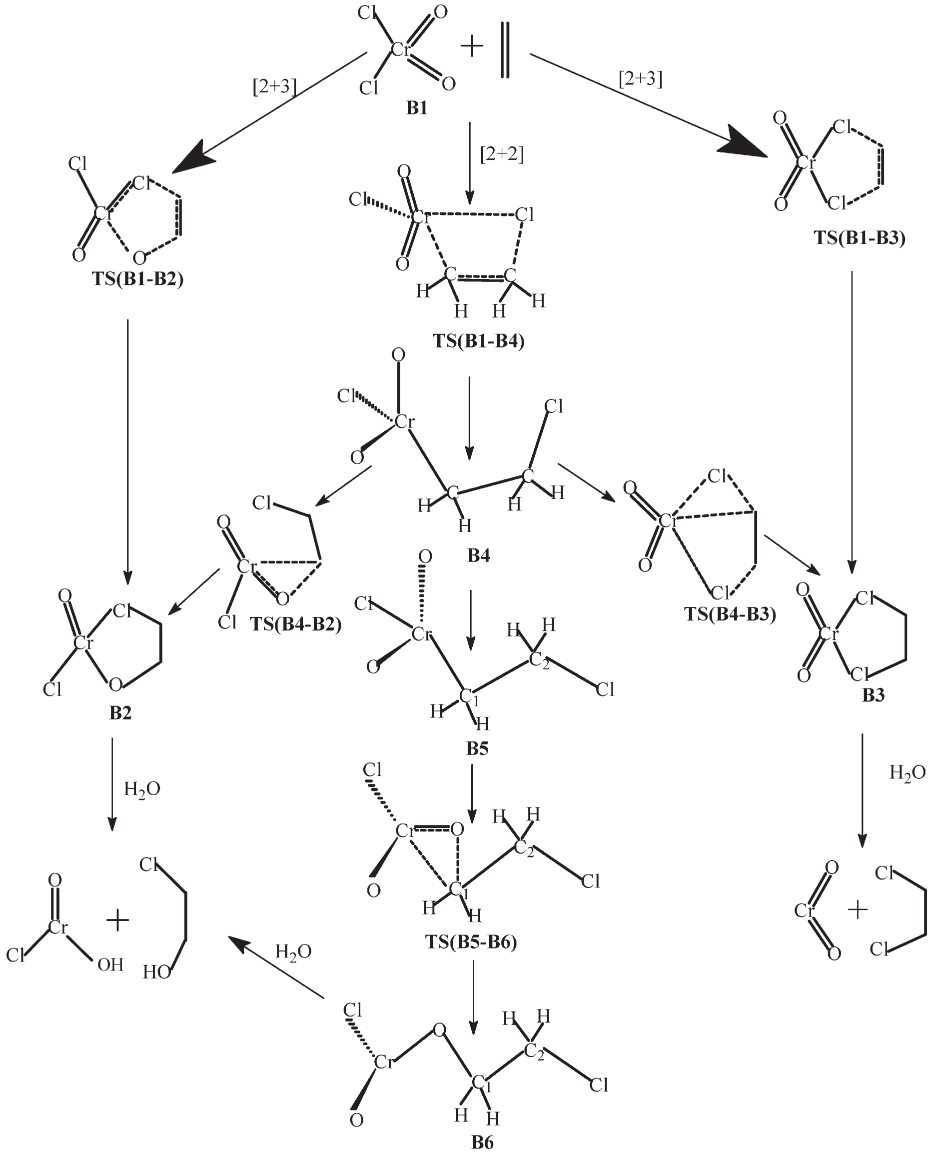
(1) a two-step process involving [2 + 2] addition of ethylene across the Cr=O bond of CrO_2Cl_2
(2) a two-step process involving [3 + 2] addition of ethylene across the two oxygen atoms of CrO_2Cl_2
(3) a two-step process involving [3 + 2] addition of ethylene across the oxygen and chlorine atoms of CrO_2Cl_2 (all shown in Scheme 4), and
(4) a one-step direct addition of ethylene to one oxygen atom of CrO_2Cl_2 (shown in Scheme 3)

No transition state was located linking the reactants and the epoxide precursor **A5** through the direct addition pathway on the singlet and triplet PES, despite an exhaustive search of the surfaces. On the basis of this, the direct addition pathway is considered a very unlikely route for epoxide formation. A triplet intermediate **C1/t** which is 0.12 kcal mol^{-1} endothermic was located and is thought to most likely arise from a direct attack of one of the olefinic carbons on an oxygen atom of CrO_2Cl_2. This intermediate rearranges through a triplet transition state **TS[C1-A3]**, with an activation barrier of 2.11 kcal mol^{-1}, to the ester complex intermediate **A3/t**. However, the transition state for the formation of **C1/t** has not been located.

Energies of the optimized molecular structures (Figures 1 and 2) obtained for the formation of epoxide and acetaldehyde precursors in Scheme 4 are summarized in the energy profile in Figure 3. Table 1 provides the imaginary frequencies (in cm^{-1}) of the first-order saddle points found in the suggested mechanism for the formation of the epoxide, acetaldehyde, dichloride, and chlorohydrin precursors.

The activation barrier for the [2 + 2] addition of ethylene across the Cr−O bonds of CrO_2Cl_2 leading to

Scheme 5. Mechanisms of the CrO_2Cl_2-Mediated Formation of Chlorohydrins and Dichlorides



the chromaoxetane **A2** is 26.31 kcal mol^{-1}, which is comparable with the 27.1 kcal mol^{-1} computed by Ziegler et al.[30] In the transition state **TS[A1-A2]**, the Cr−C forming-bond is almost completely formed whereas the C−O bond is still far from being formed. Thus the critical bond activity in **TS[A1-A2]** is the formation of the C−O bond. The forming-bonds in this transition state are slightly longer than those computed by Ziegler (by 0.032 Å for the C−O bond and 0.037 Å for the Cr−C bond). The resulting chromaoxetane adduct **A2** (singlet) is 10.28 kcal mol^{-1} endothermic (Figure 3). The endothermicity is about 4.22 kcal mol^{-1} less than that reported by Ziegler et al. No triplet **A2** was located on the surface. The formation of the epoxide precursor **A5** from the chromaoxetane intermediate **A2** through transition state **TS-[A2-A5]** has an activation barrier of 13.36 kcal mol^{-1} and an exothermicity of 20.91 kcal mol^{-1}(Figure 3). Ziegler et al.[30] found the most viable [2 + 2] second step pathway through a triplet transition state to a triplet **A5**, with an estimated activation barrier of 16.90 kcal mol^{-1} and an exothermicity of just 5.7 kcal mol^{-1}. In this work the triplet **A5** is found to be 19.54 kcal mol^{-1} more stable than the corresponding singlet state. However, the triplet **TS[A2-A5]** was not found.

The transition state **TS[A1-A4]** for the [3 + 2] addition of ethylene across the oxygen and chlorine atoms of CrO_2Cl_2 is 9.01 kcal mol^{-1} above the reactants. Species **A4** is exothermic by 17.95 kcal mol^{-1}. The formation of **A5** from **A4** through transition state **TS[A4-A5]** is 7.32 kcal mol^{-1} endothermic, with an activation barrier of 41.28 kcal mol^{-1}(Figure 3). Thus overall, the formation of **A5** by [3 + 2] addition of ethylene across the oxygen and chlorine atoms of CrO_2Cl_2 cannot compete favorably, both kinetically and thermodynamically, with formation by [2 + 2] addition.

Along the second [3 + 2] addition pathway, the transition state **TS[A1-A3]** for the formation of the ester complex intermediate is 8.76 kcal mol^{-1} above the reactants. The geometry of the transition state indicates that the addition is concerted and synchronous. Comparing the C−O bond lengths in the transition state and the product indicates that this is an early transition state. The ester complex

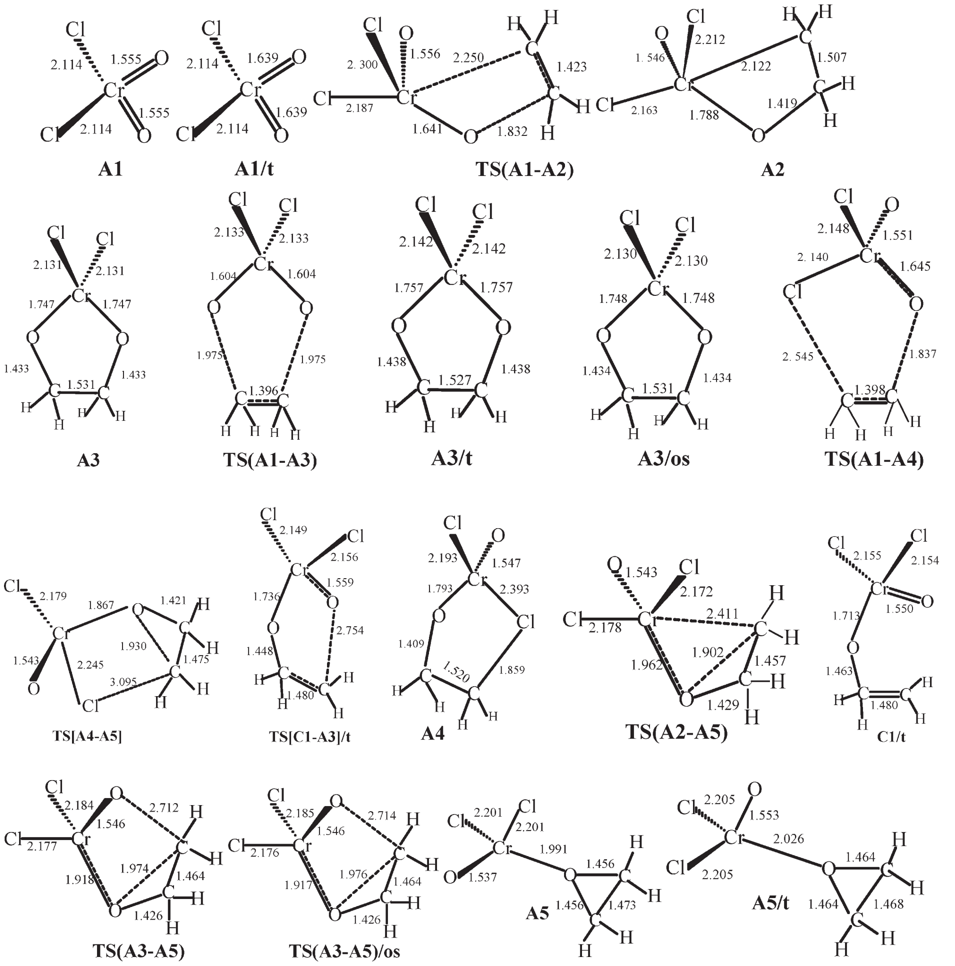


Figure 1. Optimized geometrical parameters of the main stationary points involved in the [2 + 2] and [3 + 2] addition reaction between CrO_2Cl_2 and ethylene for the formation of the epoxide precursor (*t* = triplet state, os = open-shell singlet state). Distances in Å and angles in degrees.

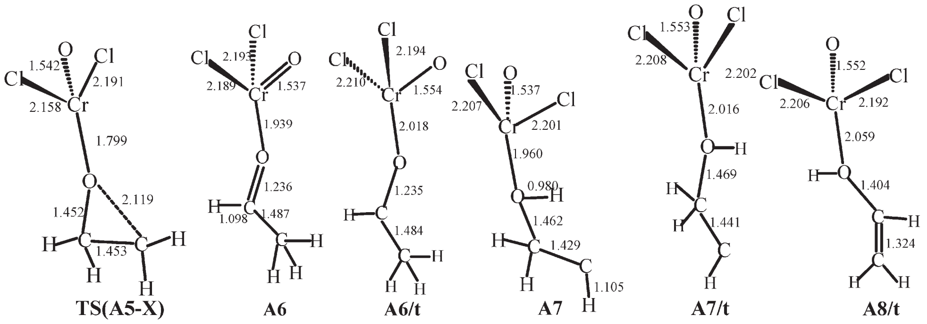


Figure 2. Optimized geometrical parameters (in Å) of the stationary points on epoxide ring-opening.

intermediate is 24.38 kcal mol^{-1} exothermic. The transition state **TS[A3-A5]** leading to the epoxide precursor from the ester intermediate is 22.61 kcal mol^{-1} above the reactants. Thus, the activation barrier for the formation of the epoxide precursor from the ester complex is 46.99 kcal mol^{-1}. Ziegler's[30] calculations found this two-step process involving the [3 + 2] interaction with activation barrier of 21.9 kcal mol^{-1} more favorable than the two-step [2 + 2] pathway that required a first step activation energy of 27.1 kcal mol^{-1}.

The present study indicates that even though in the first step of the two-step processes of epoxide precursor formation the [3 + 2] addition across two Cr═O bonds is the most favorable pathway, the ester complex intermediate **A3** formed from [3 + 2] addition is too stable to allow an easy conversion to the reputed epoxide precursor **A5**. The epoxide precursor is therefore not likely to be accessible from the ester complex intermediate. The implication of this is that the epoxide is not likely to originate from an ester intermediate formed from [3 + 2] addition, contrary to the findings of Ziegler et al.[30] On the basis of this, it is concluded that the [2 + 2] addition pathway is the preferred route for the formation of epoxide through the epoxide precursor (Figure 3). This conclusion is based on the assumption that **A3** dissipates its excess energy (exothermicity) from step 1 before it attempts to go over the second barrier. If it does not dissipate the excess

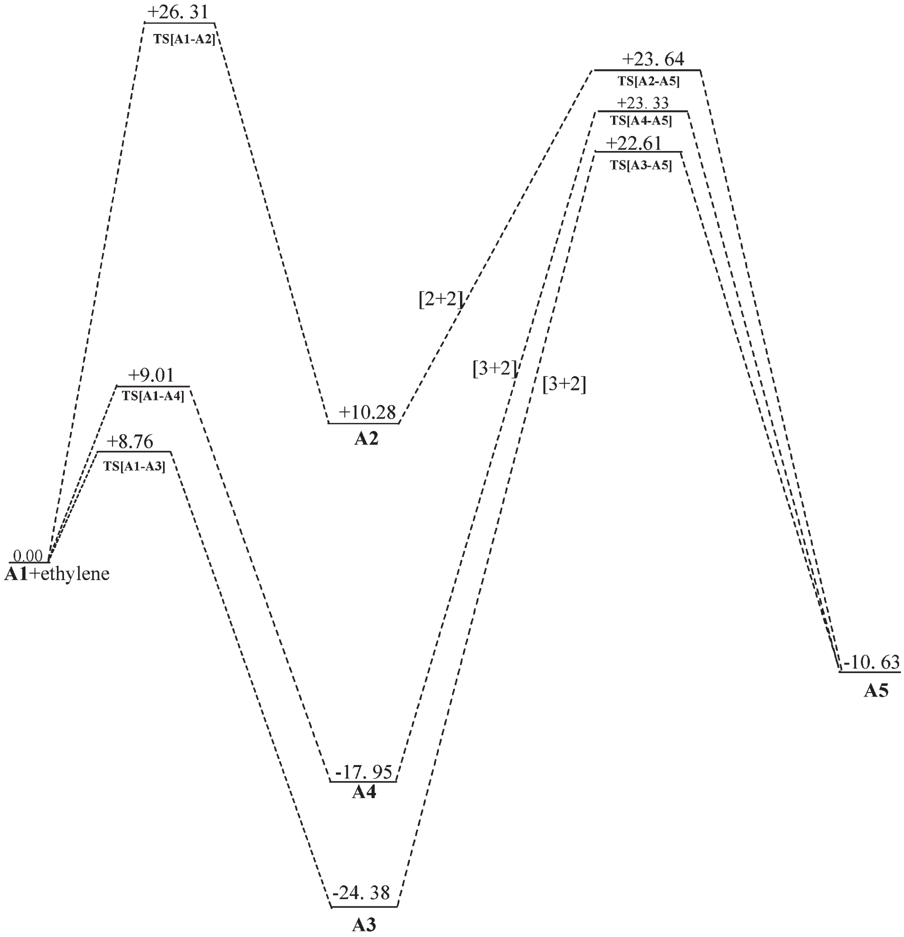


Figure 3. Reaction profile of the three suggested mechanisms for the formation of the epoxide precursor from the addition of CrO_2Cl_2 to ethylene on the singlet PES. Energy in kcal mol^{-1}.

Table 1. Imaginary Frequencies (in cm^{-1}) of All First-Order Saddle Points Involved in the Suggested Mechanisms for the Formation of Epoxide, Acetaldehyde, Dichloride and Chlorohydrin Precursors

transition state[a]	freq.
TS[A1-A2]	437.36*i*
TS[A1-A3]	432.39*i*
TS[A1-A4]	421.80*i*
TS[A2-A5]	430.71*i*
TS[A3-A5]	413.40*i*
TS[A4-A5]	402.50*i*
TS[A5-X]	294.23*i*
TS[B1−B2]	421.80*i*
TS[B1−B4]	207.99*i*
TS[B1−B3]	282.89*i*
TS[B4−B3]	332.10*i*
TS[B4−B2]	465.88*i*
TS[B5−B6]	462.07*i*

[a] Computed on a singlet PES.

energy quickly, then the [3 + 2] route via **A3** may still be the most favorable route overall.

As a result of Ziegler et al.'s[30] treatment of **A3**, **TS[A3-A5]**, and **A5** as triplet ground state species, the triplet PES was explored in relation to these species in this work. Triplet **A3** and **A5** were computed to be 49.87 kcal mol^{-1} and 30.17 kcal mol^{-1} exothermic, respectively, compared with the exothermicities of 24.3 kcal mol^{-1} and 10.63 kcal mol^{-1} found for the singlet **A3** and **A5** relative to the CrO_2Cl_2 and ethylene reactants. These exothermicities suggest that even the singlet state **A3** and **A5** intermediates should be stable enough to be observed experimentally. However, only **A5** has been observed experimentally by Limberg et al.[32] Ziegler et al. has found the triplet **A3** to be 13.0 kcal mol^{-1} exothermic and the triplet **A5** to be 8.8 kcal mol^{-1} endothermic. Ziegler's proposed mechanism for this [3 + 2] reaction leads from the singlet reactants via a singlet transition state to a triplet [2 + 3] cycloadduct **A3**, followed by rearrangement of **A3** to a triplet **A5** through a triplet transition state **TS[A3-A5]**. An exhaustive search for a triplet **TS[A3-A5]** in this work yielded no stationary point. Therefore this forbidden spin crossover path could not be fully explored.

Limberg et al.[32] did not observe in their photolytic matrix isolation experiment the intermediates **A3** and **A2** which have been proposed in the formation of the epoxide precursor **A5**, and asserting that CrO_2Cl_2 also possesses a low-lying triplet state (our calculations found the singlet more stable than the triplet) these workers concluded that if this low-lying triplet state, which was accessible in the photolytic matrix conditions, is responsible for product formation a forbidden spin crossover would not even have to be considered. Consequently the proposed[32] path was a reaction of triplet CrO_2Cl_2 with olefin in close proximity producing either epoxide **A5** or the carbonyl compounds **A6** by independent routes.

In the present work, the species **A3**, **A5**, and **TS[A3-A5]** have also been computed as open-shell singlets, and these have been found to be comparable to the closed-shell singlets in terms of both geometry and energetics (relative energies of −24.44, −10.68, and +22.61 kcal mol^{-1}, respectively).

2. Formation of Acetaldehyde and Vinyl Alcohol. Limberg et al.[31] have postulated the species **A5** as the oxirane adduct intermediate leading to acetaldehyde, upon opening of the epoxide ring. Attempts were therefore made to localize the products of epoxide ring-opening on the PES (Figure 2). The singlet and triplet transition state **TS**[**A5-X**] for epoxide ring-opening is found to be, respectively, 12.62 and 1.58 kcal mol^{-1} above the reactants. Animating the motion of the atoms along the reaction coordinate in **TS** [**A5-X**] on SPARTAN's graphical user interface reveals that in addition to breaking of the C−O bond in the three-membered ring, one of the hydrogen atoms in the carbon atom involved in the bond-breaking appears to be moving toward the oxygen atom in the three-membered ring. This leads to the formation of a carbene-like species **A7**. Triplet and singlet **A7** are 33.54 and 52.23 kcal mol^{-1} endothermic, respectively. A 1,2-hydride shift from the secondary carbon to the terminal carbon of **A7** results in species **A8**, which can undergo Cr−O single bond cleavage to produce vinyl alcohol. Triplet **A8** has been computed to be 38.01 kcal mol^{-1} exothermic while no singlet **A8** could be located. The acetaldehyde precursor **A6** has been obtained in an attempt to optimize **A8** on the singlet PES. Species **A6** has exothermicities of 40.96 and 58.20 kcal mol^{-1} for the singlet and triplet species, respectively, making it the global minimum on both the singlet and triplet PES. Limberg et al.[31] have found **A6** an intermediate in the thermal reaction of ethylene with CrO_2Cl_2 and postulated it as a precursor to the formation of acetaldehyde, upon cleavage of the Cr−O single bond. However, the most plausible pathway to the formation of **A6**, **A7**, and **A8** appears to be a direct attack of one of the carbon atoms of ethylene on an oxygen atom of CrO_2Cl_2 to form triplet **C1/t**, followed by rearrangement. The species **C1/t** and **A8** exist only on the triplet PES. Optimization of **A8** on the singlet PES converges on **A6**. Triplet **A7** (+33.52 kcal mol^{-1}) is considerably more stable than the singlet **A7** (+52.23 kcal mol^{-1}), and its high endothermicity relative to the singlet CrO_2Cl_2 and ethylene reactants suggests that it might be formed from a triplet CrO_2Cl_2 reactant.

3. Formation of 1,2-Chlorohydrin and 1,2-Dichloroethane. Sharpless et al.[2] have suggested that the conversion of olefins into chlorohydrins result from highly selective cis-addition of the elements of HOCl across the olefinic linkage, whereas chlorohydrins resulting from trans-addition were concluded to be secondary products derived by opening of the epoxide. Scheme 5 proposes three mechanistic pathways for the formation of the 1,2-dichlorohydrin, a one-step process involving [3 + 2] addition of ethylene across the oxygen and chlorine atoms of CrO_2Cl_2 to form the chlorohydrin precursor **B2**, a two-step process involving [2 + 2] addition of ethylene across the Cr−Cl bond of CrO_2Cl_2 to form the alkylchromium intermediate **B4** followed by rearrangement through **TS**[**B4**−**B2**] to **B2**, and a third route involving the formation of **B6**, which could also be considered a chlorohydrin precursor, from **B4**. In their matrix isolation studies of the reaction between CrO_2Cl_2 and ethylene, Limberg et al.[31] postulated the presence of $CrOCH_2CH_2Cl$ fragments in the Etard complex, which is consistent with the structure of **B6**.

The formation of the chlorohydrin precursor **B2** (closed-shell singlet) has been found to be 17.95 kcal mol^{-1} exothermic. An open-shell singlet **B2** has been found to be 17.96 kcal mol^{-1}, with geometrical parameters the same as those of the closed-shell singlet minimum. The activation barrier for the formation of **B2** through the [3 + 2] addition is 9.01 kcal mol^{-1} (Figure 5). In addition to the singlet **B2** which is 17.95 kcal mol^{-1} exothermic, a triplet state **B2** was computed and found to be 16.20 kcal mol^{-1} more stable than the singlet state **B2**. Ziegler et al.[30] did not report of a singlet state **B2** but found a triplet state **B2** (3.8 kcal mol^{-1} endothermic) formed from a singlet reactant **B1** via a [3 + 2] singlet transition state **TS**[**B1**−**B2**] with an activation barrier of 15.7 kcal mol^{-1} compared with a triplet activation barrier of 37.3 kcal mol^{-1}. In the two-step formation of **B2** the activation barrier for the formation of the alkylchromium intermediate **B4** is 25.61 kcal mol^{-1} (Figure 6). **B4** has been found to be 1.82 kcal mol^{-1} endothermic.

The activation barrier for the formation of **B2** from **B4** is 23.12 kcal mol^{-1}. Along the third proposed pathway for the formation of chlorohydrins (Scheme 5), species **B4** undergoes rotation about the C_1-C_2 bond to form species **B5** which is 7.89 kcal mol^{-1} more stable than **B4**. Species **B6**, which generates the chlorohydrin, is formed from **B5** by the breaking of the Cr−C bond and formation of the C−O bond. The energy barrier for this transition through **TS**[**B5**−**B6**] is 25.87 kcal mol^{-1}.

Since the [3 + 2] pathway leading to the chlorohydrin precursor **B2** has the lowest overall activation barrier and the highest exothermicity, it is concluded that the [3 + 2] route is the preferred one for the formation of 1,2-chlorohydrin from the reaction of ethylene with CrO_2Cl_2. Thus, 1,2- chlorohydrins will most likely arise from [3 + 2] addition of ethylene across the oxygen and chlorine atoms of CrO_2Cl_2 as opposed to a [2 + 2] addition pathway (Figure 5).

Chromyl chloride oxidations of olefins have also been shown to produce dichlorides in a number of cases.[2] In Scheme 5, two mechanistic pathways have been proposed to account for the formation of 1,2-dichloroethane, a [3 + 2] addition of ethylene across the chlorine atoms of CrO_2Cl_2 to form the dichloride precursor **B3** and the [2 + 2] addition of ethylene across one of the Cr−Cl bonds to form the alkylchromium intermediate **B4** followed by rearrangements through **TS**[**B4**−**B3**] to the dichloride precursor **B3**.

In the one-step [3 + 2] addition for the formation of **B3** through **TS**[**B1**−**B3**], the activation barrier for the formation of **B3** through **TS**[**B1**−**B3**] by [3 + 2] addition is 20.75 kcal mol^{-1}. The dichloride precursor **B3** (closed-shell singlet) has been found to be 17.22 kcal mol^{-1} endothermic, the open-shell singlet **B3** has also been found to be 17.21 kcal mol^{-1} endothermic while the triplet **B3** has been found to be 10.67 kcal mol^{-1} endothermic. Ziegler et al.[30] reported only a triplet minimum which was 44.7 kcal mol^{-1} endothermic and proposed a mechanism involving singlet reactants through a singlet transition state and intermediate to a triplet dichloride precursor.

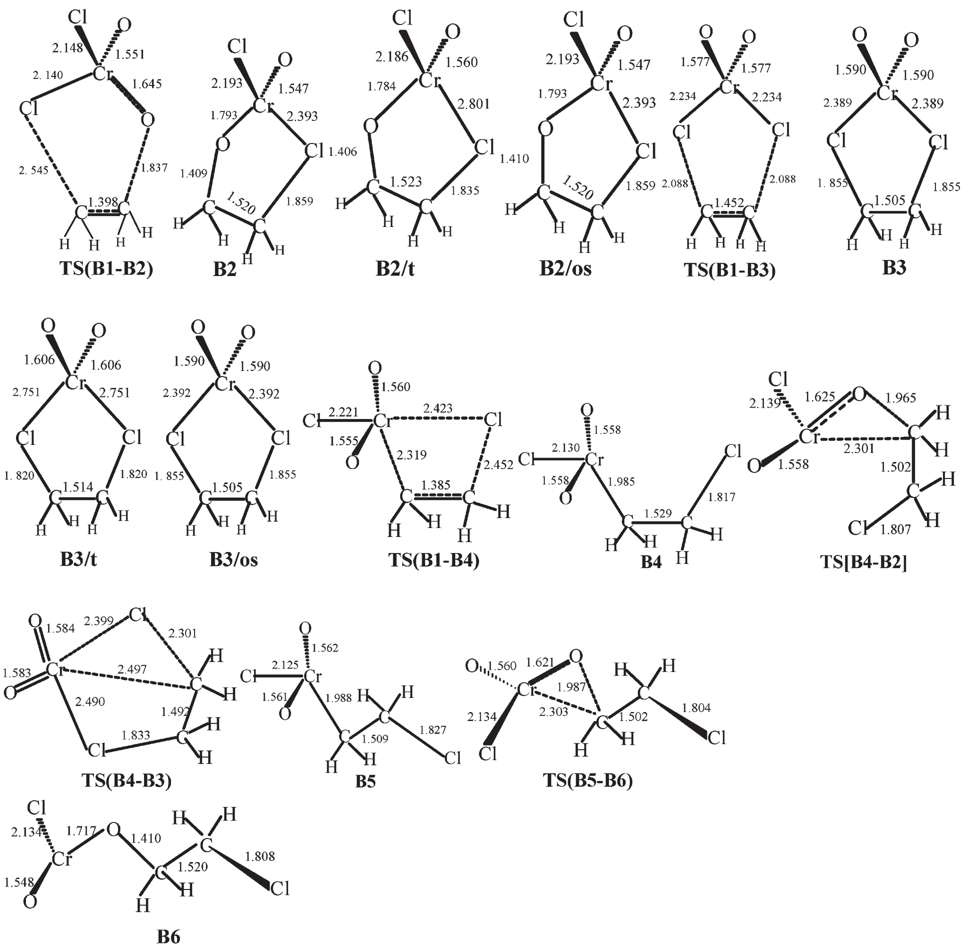


Figure 4. Optimized geometrical parameters of the main stationary points involved in the [2 + 2] and [3 + 2] addition reaction between CrO_2Cl_2 and ethylene for the formation of chlorohydrin and dichloride precursors (*t* = triplet state, os = open-shell singlet state). Distances in Å and angles in degrees.

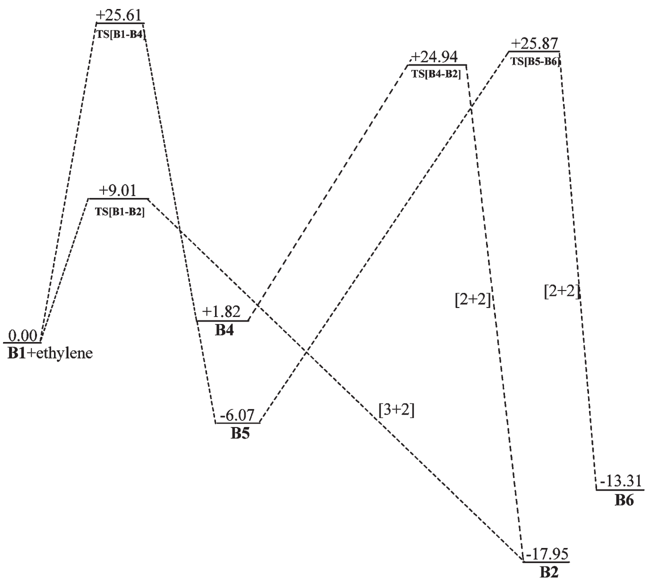


Figure 5. Energy profile of the three suggested mechanisms for the formation of the 1,2-chlorohydrin precursor from the addition of CrO_2Cl_2 and ethylene on a singlet PES. Energies in kcal mol^{-1}.

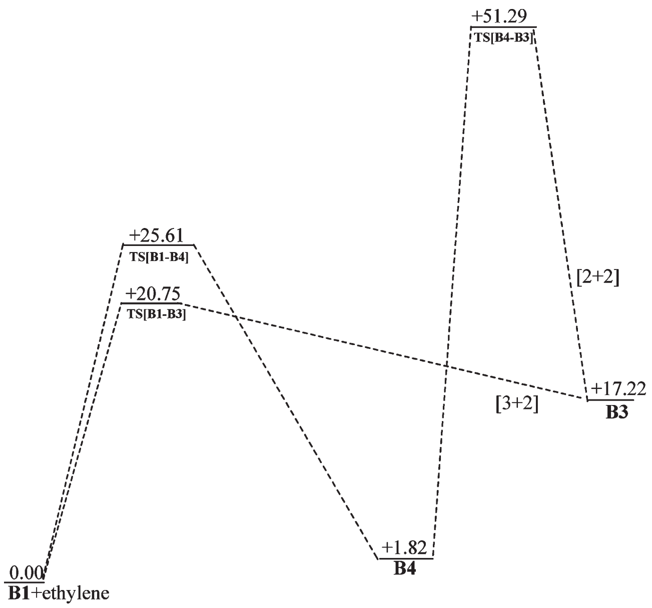


Figure 6. Energy profile of the two suggested mechanisms for the formation of the dichloride precursor from addition of CrO_2Cl_2 and ethylene on a singlet PES. Energies in kcal mol^{-1}.

In the two-step [2 + 2] addition for the formation of **B3** through **TS[B4−B3]** the activation barrier for the formation of the alkylchromium intermediate **B4** is 25.61 kcal mol^{-1}. The transition barrier linking **B4** and **B3** is very high (51.29 kcal mol^{-1}). On the basis of this energetic data (Figure 6), it is very unlikely that the dichloride precursor **B3** will originate from the [2 + 2] pathway. The [3 + 2] pathway is considered the most likely route. Furthermore, the dichloride precursor is not precluded from being formed from ethylene and CrO_2Cl_2 as the work of Ziegler et al.[30] will seem to indicate, since the formation of the dichloride precursor **B3** by [3 + 2] addition in this study is at least competitive with epoxide formation.

Conclusion

The following conclusions are drawn from the results presented:

(1) In the first step of the reaction between CrO_2Cl_2 and ethylene, the [3 + 2] addition of ethylene across the two oxygen atoms of CrO_2Cl_2 to form the ester complex intermediate has the lowest barrier (8.76 kcal mol^{-1}) compared to the [3 + 2] addition across the oxygen and chlorine atoms (9.01 kcal mol^{-1}), [3 + 2] addition across the two chlorine atoms (20.75 kcal mol^{-1}), [2 + 2] addition across the Cr−Cl bond (25.61 kcal mol^{-1}), and [2 + 2] addition across the Cr−O bond to form the chromaoxetane (26.31 kcal mol^{-1}).

(2) The most favorable pathway for the formation of the epoxide precursor is by initial [2 + 2] addition of ethylene across the Cr−O bonds of CrO_2Cl_2. The highest barrier along this pathway is 26.31 kcal mol^{-1}. The highest barrier along the [3 + 2] addition route across the oxygen and chlorine atoms is 41.28 kcal mol^{-1} while that along the [3 + 2] addition route across the two oxygen atoms is 46.99 kcal mol^{-1}. Thus, the epoxide will most likely arise from a [2 + 2] addition pathway as opposed to a [3 + 2] pathway as reported by Ziegler et al.[30]

(3) There appears to be no direct addition pathway for the formation of the epoxide precursor.

(4) The [3 + 2] addition of ethylene across the oxygen and chlorine atoms of CrO_2Cl_2, which appears to have been ignored as a plausible pathway for epoxide precursor formation in earlier studies, has been found to be favored over the [3 + 2] addition of ethylene across the two oxygen atoms of CrO_2Cl_2.

(5) The formation of 1,2-dichlorohydrin will most likely arise from [3 + 2] addition across the oxygen and chlorine atoms of CrO_2Cl_2 and not by [2 + 2] addition.

(6) The formation of 1,2-dichloroethane will most likely proceed by [3 + 2] addition of ethylene across the two chlorine atoms of CrO_2Cl_2 as opposed to a [2 + 2] addition.

(7) The 1,2-dichoroethane is not precluded from being formed from CrO_2Cl_2 and ethylene as the work of Ziegler et al.[30] may seem to indicate. The formation of dichloride is slightly favored over the formation of epoxide.

(8) The acetaldehyde precursor $O{=}CrCl_2{-}OCHCH_3$ formed from optimization of the vinyl alcohol precursor $O{=}CrCl_2{-}(OH)CH{=}CH_2$ is the most stable species on the reaction surface (40.96 kcal mol^{-1} exothermic).

(9) The vinyl alcohol precursor $O{=}CrCl_2{-}(OH)CH{=}CH_2$ has been found to exist only on the triplet PES.

(10) The inability to locate some key transition states on the triplet PES in this work does not allow a comparison of the viability of the reaction on the singlet PES and that involving the singlet−triplet ground state crossover.

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Supporting Information Available: The optimized geometries (in Cartesian and internal coordinates, in Å), absolute energies (in au) and symmetry point groups of all the structures herein reported. This material is available free of charge via the Internet at http://pubs.acs.org.