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Theoretical study on decomposition of γ-halo allylalkoxide and β-halo acrylate ions*

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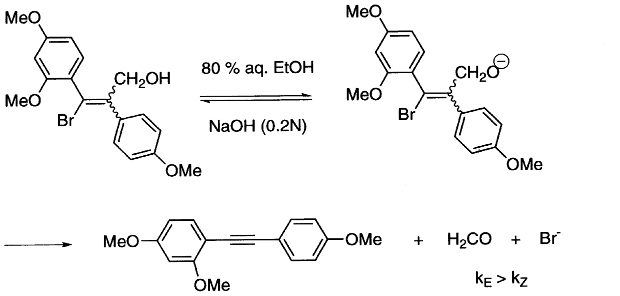
Abstract. β, γ-Substituted γ-halo allylalkoxide ions decompose to form a halogen ion, formaldehyde, and an alkyne under mild conditions, for example at room temperature. The E isomer does not differ from the Z isomer in terms of activation energy. We attempted to shed light on the mechanism of the reaction by using ab initio molecular orbital calculations. The observed propensity was confirmed by the present calculation on model molecules, γ-chloro allylalkoxide ions. We conducted further calculations and compared the alkoxide results with a similar reaction of β-haloacrylate ions that release carbon dioxide instead of formaldehyde. This similar reaction needs heating as high as 150°C. The activation energy of the acrylate ions (36–39 kcal mol^{-1}) was calculated to be about 10 kcal mol^{-1} higher than that of the alkoxide ions. The activation energy of the E acrylate ion is smaller by 0.8 kcal mol^{-1} than that of the Z isomer at the MP2/6-31+G**//RHF/6-31+G* level of theory. This is consistent with experimental results. While the ready deprotonation from the carboxylic group does not activate the acrylate ion very much, the alkoxide ion is destabilized to a great degree in the process of anion formation. The difficulty in deprotonation that proceeds from the neutral molecule is seen in the difference in the activation energies for the decomposition of the corresponding anions. Therefore, the pK_a of a hydroxy or a carboxylic group plays the leading role in determining the magnitude of activation energies of allyl halides with a negatively charged fragment.

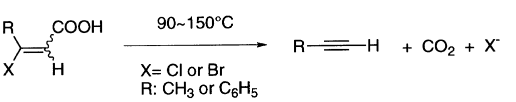
Key words: Ab initio molecular orbital calculations – Allylalkoxide ion – Acrylate ion – pK_a – Fragmentation

1 Introduction

It is well known that alkyl halides release hydrogen halides to form alkenes. The E2 mechanism has been characterized by a number of experiments [1] and investigated in detail by use of ab initio molecular orbital (MO) calculations [2]. While it is hard to find S_N2 reactions on vinylic carbon [3], elimination reactions, common occurrences from *sp*^{3} carbons, are not as common from *sp*^{2} carbons. Recently we have lighted upon such reactions in which formaldehyde is released from substituted γ-bromo allylalkoxides as shown in Eq. (1). Breaking of the C—C bond between vinyl and alkoxy fragments is accompanied by simultaneous formation of an alkyne under mild conditions, such as at 25°C. The rate of decomposition of the E isomer is faster than that of the Z isomer although the difference is not very large [4].



(1)



(2)

A similar reaction (Eq. 2) was observed in 1964 by Grob et al. [5], who used α,β-unsaturated β-halo acids and produced an alkyne and CO_2. This reaction requires a high temperature (higher than 100°C). In terms of energy, the (*E*)-β-chlorocrotonate ion ($R = CH_3$) is only 2.9 kcal mol^{-1} lower than the Z isomer, whose propensity resembles what we observed for the alkoxide system.

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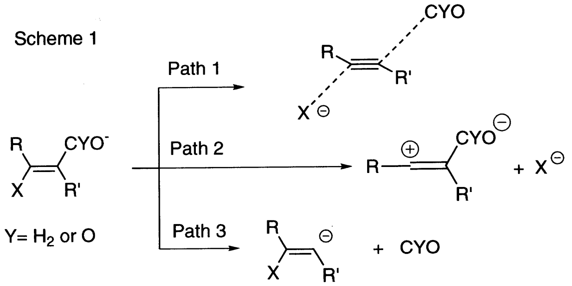
Two features are attributed to the reactions in Eqs. (1) and (2). First, they are elimination reactions to release a neutral molecule such as CH_2O or CO_2 as one of the products. Second, although E isomers decompose faster than Z isomers, the difference in rate is not as large as that in saturated systems. Reactions of E and Z isomers correspond to anti and syn elimination reactions of alkyl halides, respectively for which anti elimination predominantly proceeds if the steric effect is less important. Therefore, the propensity of reaction rates of the unsaturated ions is different from that observed in the saturated alkylhalides.

The reactions of the alkoxides may proceed under some mechanisms similar to those which Grob et al. proposed, offering three candidates shown in Scheme 1. The first candidate is a concerted one-step mechanism (path 1) in which the unsaturated anion fragments into three parts: X^-, CYO and an alkyne, where Y stands for H_2 on the alkoxide ion and for O on the carboxylate ion. The second candidate (path 2) is a two-step mechanism in which the anion initially releases X^- and forms a zwitterion with a vinyl cation fragment. The alkyne may be easily produced from this intermediate. The third candidate (path 3) is also a two-step mechanism but one via the vinyl anion without the CYO group, that departed at the first stage.

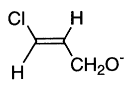
Scheme 1

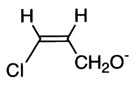


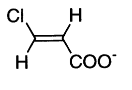
All this, however, gives rise to a number of questions as follows.

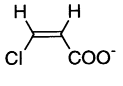
1. Which mechanism is applicable to the decomposition of the two ions, the concerted one-step or the two-step mechanism? Our preliminary calculations of model compounds, $ClHC{=}CH^-$ and $HC^+{=}CHCO_2^-$ shown in Scheme 1, failed to obtain any stable geometries; the former decomposes to acetylene and Cl^-, and the latter to acetylene and CO_2.
2. Why are Z isomers close to E isomers in terms of activation energy? It is common knowledge that anti elimination is dominant for saturated alkylhalides.
3. What factor comes in to make differences in the activation energies for the unsaturated alkoxide and carboxylate ions? Hammond's postulate [6] predicts that carboxylate ions have smaller activation energies than alkoxide ions. This is because β-halocarboxylate ions release CO_2, a chemical species more stable than CH_2O, from the γ-haloallyl alkoxide ions. However, alkoxide ions decompose at a much lower temperature than carboxylate ions which need heating up as high as 150°C.

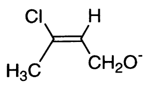
In the present study, we conducted ab initio MO calculations at the MP2/6-31 + G**//RHF/6-31 + G* level of theory to answer the above questions by using the model molecules, (*E*)- and (*Z*)-γ-chloroallyl alkoxide, 1E and 1Z, and (*E*)- and (*Z*)-β-chloroacrylate ions, 2E and 2Z. The substitution at the β or γ position in 1E and 1Z is related to the activation energies of the reaction and this necessitated the adoption of molecules of such sort for our experiments. Thus, calculations were also performed on the isomers 3E~4Z, in which either of the hydrogen atoms on the double bond is substituted by a methyl group.

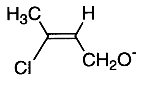

1E

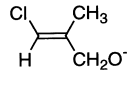

1Z

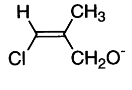

2E


2Z


3E


3Z


4E


4Z

2 Method of calculation

Ab initio MO calculations were performed using the GAUSSIAN94 program [7] to optimize stable and transition state (TS) structures. The 6-31 + G* [8] basis sets equipped with both diffuse and polarization functions were adopted. The vibration frequencies were calculated on all of the molecules to see whether they are at a stationary point or at a TS. A summary of all the energies and geometrical parameters obtained is provided in Tables 1 and 2. More calculations were done on the intrinsic reaction coordinate (IRC) [9] for 1E, 1Z, 2E, and 2Z to shed light on a more detailed reaction mechanism. The MP2/6-31 + G** [10] calculations were also done to obtain better energy descriptions among the related molecules. As we shall discuss later, to describe the proper order of the activation energies for decomposition the correlation effect needs to be considered. The energies mentioned in section 3 were used at the MP2/6-31 + G**//RHF/6-31 + G* level of theory unless otherwise noted.

3 Results and discussion

3.1 Geometrical features of β-chroloallyl alkoxide ions and their TSs

Two structures, which are conformational isomers shown in Fig. 1 together with Cl(1)—C(2) and C(3)—C(4) lengths, were obtained for γ-chroloallyl alkoxide with the E configuration. One is structure 1E(1), where all the heavy atoms sit on an almost level plane, with atoms O(5) and H(6) sitting 2.531 Å apart from each other. The other is structure 1E(2), where O(5) protrudes from the plane that H(8) and the other heavy atoms make; hence the C(2)—C(3)—C(4)—O(5) angle is −128.8°. Calculations of Cl(1)—C(2) lengths for 1E(1) and 1E(2) produced the same value of 1.778 Å as

Table 1. Total energies and geometrical parameters[a] optimized for the decomposition of β-chloro allyl alkoxide ion and γ-chloro arylalkoxide

	1E(1)	1E(TS1)	1E(2)	1E(TS2)	1Z	1Z(TS)	2E	2E(TS)	2Z	2Z(TS)
RHF/6-31 + G*[b]	−650.22271	−650.18488	−650.22023	−650.18495	−650.21673	−650.18175	−724.01213	−723.95393	−724.00042	−723.94609
E[c,d]	0.0	23.7	1.6	23.7	3.8	25.7(21.9)	0.0	36.5	7.3	41.4(34.1)
MP2/6-31 + G**[b]	−650.96986	−650.92878	−650.96722	−650.92862	−650.96206	−650.92197	−724.90737	−724.84695	−724.89833	−724.83661
E[c,d]	0.0	25.8(25.8)	1.7	25.9(25.9)	4.9	30.1(25.2)	0.0	37.9(37.9)	5.7	44.4(38.7)
C(2)—C(3)	1.314	1.303	1.317	1.305	1.320	1.315	1.314	1.293	1.318	1.317
C(3)—C(4)	1.535	2.314	1.535	2.280	1.540	2.314	1.542	2.545	1.539	2.586
Cl(1)—C(2)	1.778	1.896	1.778	1.902	1.769	1.845	1.766	1.995	1.750	1.849
C(4)—O(5)[e]	1.320	1.217	1.320	1.220	1.330	1.219	1.233,1.233	1.155,1.154	1.227,1.235	1.153,1.153
C(2)—C(3)—C(4)	121.8	111.8	125.1	130.6	131.4	135.4	121.8	118.5	131.0	132.1
C(2)—C(3)—H(7)	120.0	116.9	120.0	117.7	115.5	110.2	121.2	118.2	114.8	107.1
C(3)—C(2)—H(6)	123.8	129.8	125.4	130.9	125.6	121.2	123.9	134.9	122.8	133.1
Cl(1)—C(2)—C(3)	113.2	125.1	123.5	125.2	123.4	121.2	123.3	124.3	126.2	121.8
C(2)—C(3)—C(4)—O(5)	0.0	180.0	−128.8	−180.0	180.0	180.0	180.0	180.0	−43.8	−90.4

[a] Bond length in angstroms and angles in degrees

[b] Total energy in hartrees at the RHF/6-31 + G* and MP2/6-31 + G**//RHF/6-31 + G* level of theory

[c] Energy difference in kcal mol^{-1} from 1E(1) or 2E in kcal mol^{-1}

[d] Values in parentheses are the activation energies for each reaction

[e] C(4)—C(5) and C(4)—O(8) lengths for 2E and 2Z

listed in Table 1. The calculated value comes close to the observed value for vinyl chloride (1.730 Å) [11]. The geometrical parameters in both structures are very close to each other except that O(5) differs in direction.

As shown in Fig. 1, two TS geometries, 1E(TS1) and 1E(TS2), were also obtained, still retaining the original geometrical characteristics of the primordial molecules. Bond C(3)—C(4) at the TS was 2.314 and 2.280 Å in length, elongated by as long as 0.779 and 0.745 Å from 1E(1) and 1E(2), respectively. On the other hand, the Cl(1)—C(2) distance of both structures at the TSs proved to be 1.896 and 1.902 Å, these distances being lengthened by no more than 0.118 and 0.124 Å from the stable structures. Although both conformers of 1E(TS) lose the CH_2O fragment at the TSs, the Cl fragment still retains the bond with the acetylene fragment. As the C(2)—C(3)—H(7) fragment takes the bent geometry shown in Scheme 1, these TS structures possess the feature of the vinyl anion with a weakly interacting CH_2O.

As regards the geometrical parameters, 1Z is close to 1E(1) and 1E(2) except for the C(2)—C(3)—C(4) angles which are 131.4°, 121.8°, and 125.1°, respectively. The angle for 1Z deviates greatly from the sp^2 angle. In this isomer, O(5) and Cl(1) are structured so as to avoid steric repulsion between the two atoms. 1Z(TS) also inherits the original geometrical structure. Bond Cl(1)—C(2) was 1.845 Å in length, which was longer only by 0.076 Å than in 1Z. The length of C(3)—C(4) in 1Z(TS) was almost as long as that of the 1E(TS): it was 2.314 Å long.

At the MP2/6-31 + G**//RHF/6-31 + G* level of theory, 1E(1) is more stable than 1E(2) by 1.7 kcal mol^{-1} and the weak O(5)—H(6) interaction stabilizes 1E(1) but to a slight degree. The activation energy of 1E(1) was 25.8 kcal mol^{-1}.[1] As the positions of the two fragments Cl and CH_2O determine the relative stability between the E and Z isomers, 1Z is less stable than 1E(1) by 4.9 kcal mol^{-1}. The activation energy for 1Z was calculated to be 25.2 kcal mol^{-1} which was 0.7 kcal mol^{-1} lower than for the E isomer. Although the difference in the activation energies is very small, the propensity is not consistent with the experimental results which assert that E isomers decompose faster than Z isomers. As we shall discuss later, the substitution that occurs at the β position largely affects the activation barrier. We always used alkoxide ions with substitutions at the positions in question when the experiments were carried out.

As we have discussed, the first geometrical change is the elongation of bond C(3)—C(4). It follows, therefore, that our consideration can be reduced to two types of orbital interactions relevant to the cleavage of bonds C(3)—C(4) and Cl(1)—C(2). Schematic orbital interactions of E and Z alkoxide ions are shown in Fig. 2. For both isomers, interaction $n_{\mathrm{o}} \rightarrow \sigma^*_{\mathrm{C-C}}$ is to be considered,

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[1] We obtained two types of geometry for 1E, 3E, and 4E including their TS. It is possible to calculate two activation energies, i.e., from 1E and 1E(TS), and from 1E and 1E(TS2). We adopted a smaller value as the activation energy for the decomposition of the E isomer

Table 2. Total energies and geometrical parameters[a] optimized for decomposition of α- or β-methyl substituted β-chloro allyl alkoxide ions

	3E(1)	3E(TS1)	3E(2)	3E(TS2)	3Z	3Z(TS)
RHF/6-31G*[b]	−689.26090	−689.22529	−689.25599	−689.22309	−689.25474	−689.21875
E[c,d]	0.0	22.3(22.3)	3.1	23.7(23.7)	3.9	26.4(22.5)
MP2/6-31G**[b]	−690.16005	−690.12104	−690.15339	−690.11869	−690.15172	−690.10995
E[c,d]	0.0	24.5(24.5)	4.2	26.0(26.0)	5.2	31.4(26.2)
C(2)—C(3)	1.319	1.254	1.319	1.300	1.320	1.314
C(3)—C(4)	1.541	2.432	1.552	2.272	1.541	2.328
Cl(1)—C(2)	1.812	1.936	1.796	1.958	1.784	1.872
C(4)—O(5)	1.321	1.247	1.325	1.220	1.331	1.218
C(2)—C(3)—C(4)	128.1	114.4	127.3	130.1	131.6	110.6
C(2)—C(3)—H(7)	117.5	129.0	119.6	118.6	115.9	110.6
C(3)—C(2)—C(6)	129.6	147.7	127.9	132.7	127.7	134.5
Cl(1)—C(2)—C(3)	118.0	113.0	120.1	121.5	120.4	118.0
C(2)—C(3)—C(4)—O(5)	0.0	0.0	−180.0	−180.0	180.0	−180.0
	4E(1)	4E(TS1)	4E(2)	4E(TS2)	4Z	4Z(TS)
Total energy[b]	−689.26077	−689.22206	−689.26019	−689.22425	−689.25610	−689.21940
E[c,d]	0.1	24.4(24.4)	0.4	23.0(23.0)	3.0	26.0(23.4)
Total energy[b]	−690.15958	−690.11795	−690.15920	−690.12196	−690.15401	−690.10904
E[c,d]	0.3	26.4(26.4)	0.5	23.9(23.9)	3.8	32.0(28.2)
C(2)—C(3)	1.316	1.287	1.320	1.283	1.324	1.315
C(3)—C(4)	1.546	2.313	1.550	2.262	1.547	2.436
Cl(1)—C(2)	1.781	1.989	1.783	2.030	1.772	1.836
C(4)—O(5)	1.316	1.216	1.325	1.221	1.330	1.213
C(2)—C(3)—C(4)	118.3	127.4	120.0	121.6	127.9	132.2
C(1)—C(2)—C(7)	124.4	133.6	125.6	128.8	117.9	115.5
C(3)—C(2)—H(6)	123.2	133.6	124.3	136.4	125.0	131.6
Cl(1)—C(2)—C(3)	123.5	124.4	125.4	123.8	124.8	121.9
C(1)—C(2)—C(3)—O(5)	0.0	0.0	−129.6	0.0	0.0	0.0

[a] Bond length in angstroms and angles in degrees

[b] Total energy in hartrees at the RHF/6-31 + G* and MP2/6-31 + G**//RHF/6-31 + G* level of theory

[c] Energy difference from 3E(1) in kcal mol^{-1}

[d] Values in parentheses are the activation energies for each reaction path

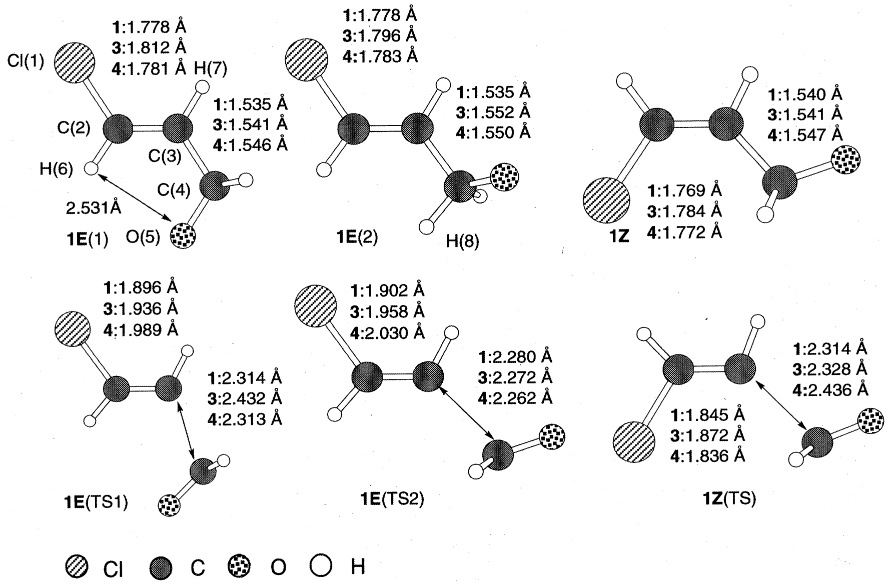


Fig. 1. Optimized geometries of *1E(1)*, *1E(2)*, *1Z* and their corresponding transition states (*TSs*) for the decomposition. *Upper*, *middle*, and *bottom lines* of atom distances are the lengths of 1, 3 and 4, respectively

where n_o stands for the lone-pair orbital of O(5) and σ^*_{C-C} for the antibonding orbital of bond C(3)—C(4). The interaction weakens bond C(3)—C(4) at the initial stage of the reaction. The cleavage of the bond in turn forms a lone pair orbital n_C on C(3), and this is followed by interaction $n_C \rightarrow \sigma^*_{C-Cl}$, which leads to the breaking of bond Cl(1)—C(2). Similar orbital interactions are again to be considered for 1Z.

3.2 Substitution effect on β or γ positions of allyl alkoxide

The substitution at either the β or the γ position of γ-chloroallyl alkoxide ion introduces changes in the geometrical parameters for both stable and TS structures. A methyl group is fixed at the γ position on 3 or at the β position on 4. Table 2 summarizes optimized parameters whose lengths Cl(1)—C(2) and

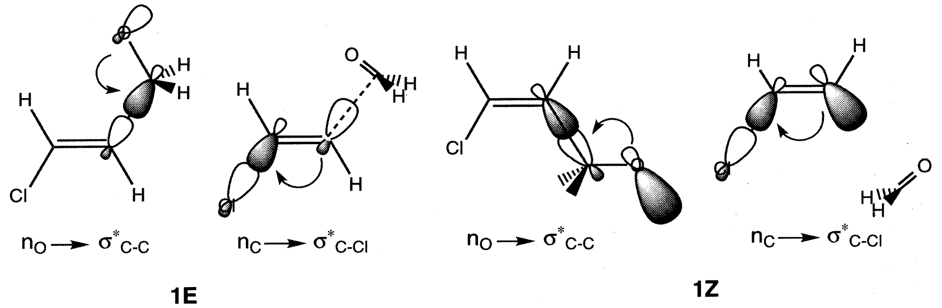


Fig. 2. Schematic representation of orbital interactions in *1E* and *1Z*

C(3)—C(4) are also listed in the middle and bottom lines in Fig. 1.

The Cl(1)—C(2) lengths in 3Z(TS) and 4Z(TS) (1.872 and 1.836 Å) are not far from those obtained for 1Z(TS), where they are longer by 0.027 and shorter by 0.009 Å, respectively. The C(3)—C(4) lengths in both TSs are longer than that of 1Z(TS). Therefore, these TSs with Z conformations are characterized as the geometries in which vinyl anion weakly interacts with CH_2O. Although we obtained no stable structures of vinyl anion intermediates, these results suggest a mechanism via a vinyl ion intermediate for the Z isomer.

In terms of bond Cl(1)—C(2), 3E(1) is longer by 0.034 Å than 1E(1), the most extreme deviation in length of all the stable structures. This deviation is caused by the methyl substitution on the parent molecules. In contrast to 1E(TS1), 3E(TS1) is characterized by a longer Cl(1)—C(2) distance (1.936 Å), where the linking bond is missing between the two atoms, and by a longer C(3)—C(4) (2.432 Å), which is longer by 0.118 Å. At the TSs, the two ions have already decomposed into three parts, Cl^-, acetylene, and CH_2O. Although the fragmentation of the ion is almost complete, angle C(2)—C(3)—H(7) is 129.0° in 3E(TS1) as listed in Table 2 and, therefore, the acetylene fragment still does not lose its original sp^2 nature. The methyl substitution at the γ position enhances the concerted nature of the reaction, viz., a simultaneous breaking of bonds Cl(1)—C(2) and C(3)—C(4). The same propensity is seen in 4E(TS). Both the γ and β substitutions also have great influence on the reaction mechanism of the E allylalkoxide.

At the MP2/6-31+G**//RHF/6-31+G* level of theory, 3E(1) is more stable than 3Z by 5.2 kcal mol^{-1} as expected. A similar difference is observed between 1E(1) and 1Z, and this means that the γ substitution does not affect the relative stability of the stable structures of the two isomers. On the other hand, the energy difference between 3E(TS1) and 3Z(TS) is 6.9 kcal mol^{-1}, which turned out to be larger by 4.3 kcal mol^{-1} than the corresponding value for the unsubstituted system, suggesting that γ substitution stabilizes the TS of the E isomer better than the Z isomer. The activation energy for 3E was calculated to be 24.5 kcal mol^{-1} and for 3Z to be 26.2 kcal mol^{-1}. The E isomer has an activation energy 4.6 kcal mol^{-1} smaller than the Z isomer. This propensity is consistent with what we observed in experiments [4].

4E(1) is more stable than 4Z by 3.5 kcal mol^{-1} and less stable than 3E(1) by 0.5 kcal mol^{-1}. The β substitution enhances the stability of the TS for the E isomer. The energy difference between 4E(TS2) and 4Z(TS) was 9.9 kcal mol^{-1}. Calculations on the activation energies for 4E and 4Z yielded values of 23.9 and 28.2 kcal mol^{-1}, respectively. The order of the activation energy was also consistent with the experimental results.

3.3 Geometrical features of γ-chloroacrylate ions and their TSs

In terms of the geometrical parameters in fragment ClHC=CH, 2E and 2Z are not very different from 1E and 1Z as the list in Table 1 suggests. Stable and TS structures of 2E and 2Z are shown in Fig. 3. All of the atoms in 2E stay level on the same plane so that the chlorovinyl fragment can conjugate with fragment CO_2. Cl(1)—C(2) in 2E(TS) is 1.995 Å long and is longer by 0.099 Å than the corresponding lengths in 1E(TS1). The length of C(3)—C(4) for 2E(TS) was calculated to be 2.545 Å which is longer by 0.231 Å than that of 1E(TS1). Therefore, 2E(TS) has the nature of a TS under the concerted mechanism as seen in 3E(TS1).

On the other hand, fragment CO_2 in 2Z stands outside the conjugation with the chlorovinyl fragment because the dihedral angle C(2)—C(3)—C(4)—O(5) is −48.3°. Angle C(2)—C(3)—C(4) is as wide as 131.0°. This structure is, however, convenient to avoid the steric repulsion between fragments Cl and CO_2. Length

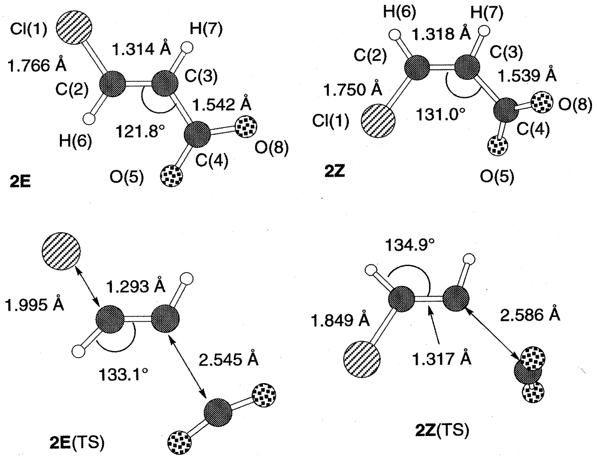
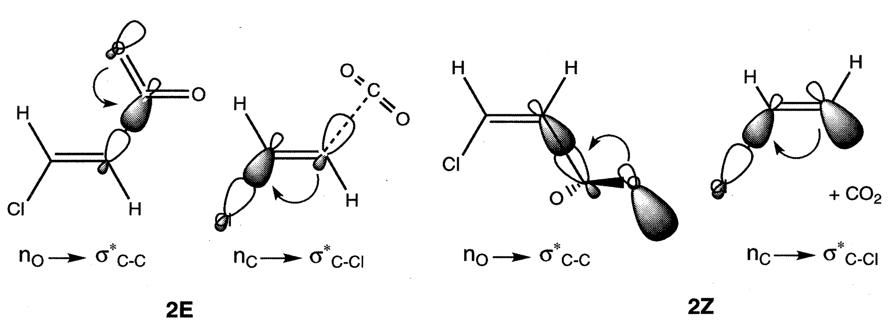


Fig. 3. Optimized geometries and geometrical parameters of *2E*, *2Z* and their corresponding TSs for the decomposition

Fig. 4. Schematic representation of orbital interactions in *2E* and *2Z*



Cl(1)—C(2) of 2Z(TS) is 1.849 Å, almost as long as 1Z(TS) (1.845 Å). Both the TSs do not lose the sp^2 nature of C(2) because angles C(3)—C(2)—H(6) are 133.1° and 134.9°, respectively. The length of C(3)—C(4) for 2Z(TS) is calculated to be 2.586 Å, which is longer by 0.272 Å than the corresponding values in the allylalkoxide ion. Since the dihedral angle C(2)—C(3)—C(4)—O(5) in 2Z(TS) is −90.6°, fragment O=C=O is perpendicular to plane Cl(1)—C(2)—C(3). Therefore, 2Z(TS) has vinyl anion nature.

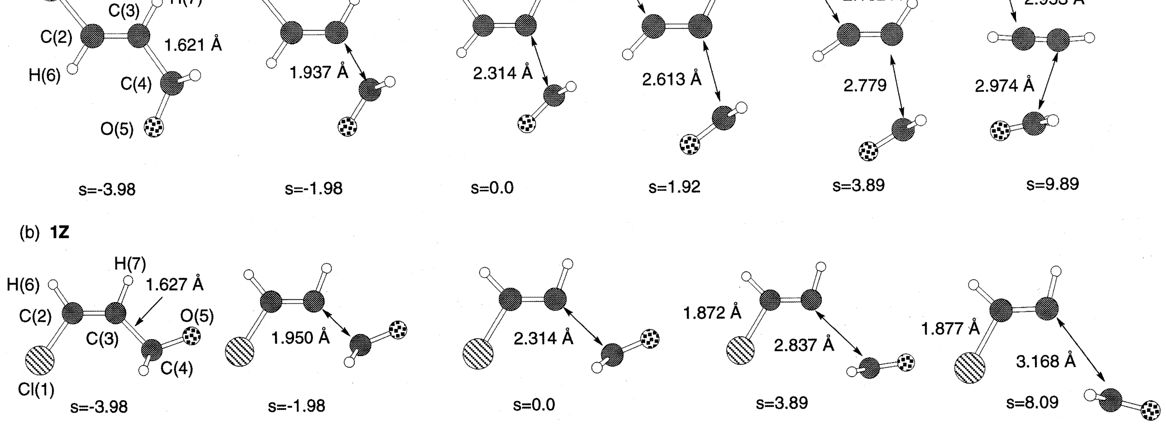
At the MP2/6-31 + G**//RHF/6-31 + G* level of theory, 2E is more stable than 2Z by 5.7 kcal mol^{-1}. In addition 2E(TS) is more stable than 2Z(TS) by 6.5 kcal mol^{-1}. The calculated activation energies for 2E and 2Z were 37.9 and 38.7 kcal mol^{-1}, respectively. The observed activation energies for (*E*) and (*Z*)-*β*-chloro crotonate ions are 33.9 and 36.8 kcal mol^{-1}, respectively. In spite of the lack of substituents at both *α* and *β* positions in our models, the calculated values come very close to the observed ones: this is consistent with the propensity pertinent to these observed activation energies. At the RHF/6-31 + G* level of theory, 2E possesses an activation energy 2.4 kcal mol^{-1} larger than 2Z. The necessity arises to include correlation effects to describe the proper order of activation energies for the acrylate system.

Since 2E and 2Z have lone pair orbitals on the carboxylic oxygens, we can consider orbital interactions similar to 1E and 1Z. Two types of orbital interactions are conceivable for the crotonate ions as shown in Fig. 4: one being the interaction $n_o \rightarrow \sigma^*_{C-C}$ that bears close resemblance to that in 1E; the other interaction is the charge transfer that occurs from n_C to σ^*_{C-Cl}. The latter interaction is more effective in the E isomer than in the Z isomer because, at the TS, the length of Cl(1)—C(2) of 2E(TS) is much longer than that of 2Z(TS).

3.4 The IRCs for decomposition of the unsaturated ions with an anionic fragment

In order to discuss the reaction mechanism in detail, the IRCs of the ions were calculated. Figure 5a illustrates the change of the geometry of 1E(1) along the IRC. Although bond C(3)—C(4) is 1.621 Å long at $s = -3.98$ amu$^{1/2}$ bohr, its geometry is similar to that of 1E(1). At $s = 3.89$ amu$^{1/2}$ bohr, 1E(1) has already decomposed into CH_2O, Cl^-, and C_2H_2 because of the lengths of C(3)—C(4) and Cl(1)—C(2) which are, by estimation, 2.779 and 2.162 Å, respectively. At this point on the IRC, the last fragment possesses a bent structure dissimilar to the linear structure of the final product, acetylene. This fragment is almost linear at $s = 9.89$ amu$^{1/2}$ bohr. Therefore, 1E(TS1) is identified as the TS for the mechanism that connects 1E(1) to the fragmentation products under the concerted mechanism

Fig. 5. Change of geometries of decomposition of **a** E and **b** Z isomers of *β*-chloroallyl alkoxide ion along the intrinsic reaction coordinate



although the TS geometry does not have a clear feature for the concerted mechanism.

The IRC of 1Z, which is displayed in Fig. 5b, shows different features. Although bond C(3)—C(4) (1.627 Å) is a little long in comparison with that in the optimized structure, the geometry at $s = -3.98$ amu$^{1/2}$ bohr is close to that of 1Z. Along the IRC, this bond becomes longer while the Cl(1)—C(2) length is almost unchanged. For example, at $s = 3.89$ amu$^{1/2}$ bohr, the C(3)—C(4) distance is longer by 1.298 Å than that in the stable structure, while the Cl(1)—C(2) length only increases by 0.112 Å. At this point, the chlorovinyl fragment still has sp^2 hybridization at C(3) because the angle C(2)—C(3)—H(7) is 107.0°. Even in the geometry at $s = 8.09$ amu$^{1/2}$ bohr, this angle is 106.3° and the Cl(1)—C(2) bond (1.877 Å) still exists; a vinyl ion weakly interacts with CH_2O. The IRC calculations for 1Z clearly indicate that the Z isomer decomposes via the vinyl anion intermediate. As already mentioned, the preliminary calculation of the anion failed to optimize the anion intermediate and, therefore, the anion formed easily decomposes into Cl^- and acetylene.

It was confirmed from the IRC calculations for 2E and 2Z that the TSs obtained connect the reactants and products.

3.5 Difference of reactivity between allyl alkoxide and acrylate ions

The last question is why the acrylate ions have larger activation energies than the alkoxide ions although the former produces CO_2 much more stably than the latter produces CH_2O. Hammond's postulate [6] expects that a reaction with stable products has a lower activation energy than that with unstable products. This is true when their neutral forms are regarded as the reactants.

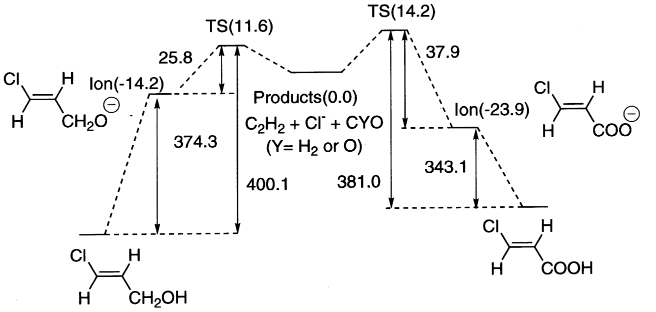


Fig. 6. Energy diagram for decomposition of the allylalkoxide and the acrylate ions. The energies in kcal mol^{-1} were estimated at the MP2/6-31 + G**//RHF/6-31 + G* level of theory. Values in parentheses are the energies relative to the products

(*E*)-β-chloroacrylic acid and its TS differ in energy by 381.0 kcal mol^{-1} while the energy for (*E*)-γ-chloroallyl alcohol is 400.1 kcal mol^{-1} as shown in Fig. 6.[2] The energy for the acid is smaller by 19.1 kcal mol^{-1} than that for the alcohol although these energies are not the activation energies of decomposition of the ions. The energy difference means that acrylic acid is more reactive than allyl alcohol, being consistent with the postulate. For the corresponding ions, however, the order of the activation energies, which were confirmed by experiments and estimated by present calculations, is not consistent with that expected from the postulate.

The decompositions of (*E*)-γ-chloroallyl alkoxide and (*E*)-β-chloroacrylate ions, 1E and 2E, were endothermic by 14.2 and 23.9 kcal mol^{-1}. The alkoxide ion was less endothermic than the acrylate ion even though the latter anion releases a stable CO_2 molecule as the product. This result leads us to expect that 1E needs a lower activation energy for decomposition than the acrylate ion does. The activation energy for 2E was estimated to be larger than that for 1E by 12.1 kcal mol^{-1}. This result is consistent with experiments. The stability of the neutral products, CO_2 and CH_2O is irrelevant to the barrier height of the reactions.

The pK_a values of functional groups are related to the magnitude of the deprotonation energy. For example, the magnitude of the pK_a of the hydroxy group in alcohol is as large as 16 and, therefore, the alkoxide ion formed is made far more unstable than the original alcohol. On the other hand, a proton is easily released from the carboxylic group due to the small magnitude of the pK_a value for the carboxy group: as small as 4.5. It is seen that the pK_a values correlate well to the calculated values of the energy difference between neutral and anion forms. The calculated energy difference between 1E(1) and (*E*)-γ-chloroallyl alcohol was 374.3 kcal mol^{-1}. This value is larger by 41.2 kcal mol^{-1} than the value of 343.1 kcal mol^{-1} between 2E and (*E*)-β-chloroacrylate acid. This means that deprotonation destroys the stability of the alcohol much more than the acrylic acid, and the alkoxide anion is activated to an enormous extent.

It is necessary to emphasize that large energy differences are not directly concerned with the decomposition of the ions. Experiments were performed in basic conditions with OH^- ions. The OH^- ion easily reacts with alcohol to produce an alkoxide ion as follows:

$$ROH + OH^- \rightarrow RO^- + H_2O. \tag{3}$$

This reaction is exothermic, that is, $RO^- + H_2O$ is more stable by 21.6 kcal mol^{-1} than $ROH + OH^-$. The value is smaller by 30.9 kcal mol^{-1} than the corresponding value (52.5 kcal mol^{-1}) for the E acrylic acid. The Experimental conditions for allyl alcohol induce deprotonation which lifts the starting point of the decomposition.

The activation energy for decomposition is related to the parent molecule's readiness to release a proton. Therefore, the starting stage of the ions is the key to lowering the activation energies for the alkoxide ions observed. It seems to be possible to have control over the activation energies for the decomposition of ions by picking out an anionic group with a different pK_a in the molecules.

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[2] The total energies (*E*)-β-chloroacrylic acid and (*E*)-γ-chloroallyl alcohol were estimated to be −651.56632 and −725.45419 hartrees at the MP2/6-31 + G**//RHF/6-31 + G* level of theory

4 Concluding remarks

The present study has been an attempt to shed light on the mechanism of the decomposition of γ-haloallyl alkoxide and β-haloacrylate ions, using model systems loaded with ab initio MO calculations. We can summarize the findings of our theoretical study as follows.

1. Both alkoxide and carboxylate ions without substituents release CH_2O or CO_2 at the beginning of the reaction. The E alkoxide ion with a methyl group releases Cl^- and CH_2O simultaneously, that is to say, the reaction proceeds under a concerted mechanism. On the other hand, Z isomers decompose via a vinyl anion intermediate.
2. The activation energy for decomposition is considerably influenced by the substituent of the unsaturated fragment. Correlation effects have to be included in order to have the proper order of the observed activation energies.
3. The activation energies of the acrylate ions are larger than those of the allyl alkoxide ions by about 15 kcal mol^{-1}. This is consistent with the experimental results that the acrylate ions require a higher temperature to decompose.
4. The pK_a value for the anion fragment is closely related to the magnitude of the activation energies for decomposition.

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