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Enhanced Reactivity of $RC{\equiv}CZ^-$ (R = H and Cl; Z = O, S, and Se) and the Influence of Leaving Group on the α-Effect in the E2 Reactions

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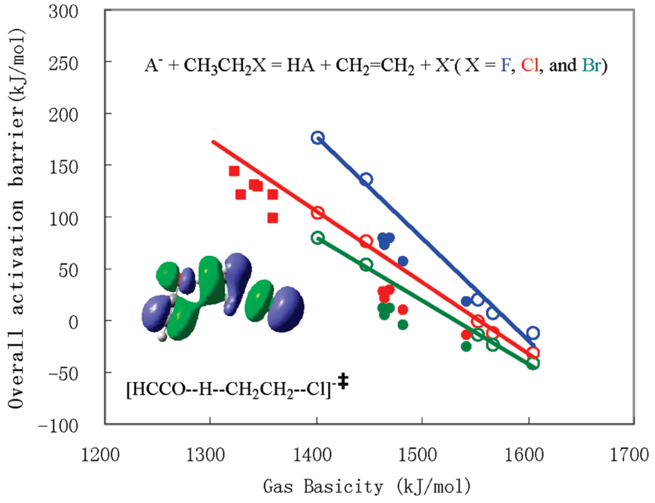

The enhanced reactivity exhibited by six pseudo-α-bases, $RC{\equiv}CZ^-$ (R = H and Cl; Z = O, S, and Se) in gas-phase E2 reactions with ethyl chloride was examined at the G2(+) level. It is found that anomalous reactivity is observed despite the fact that these chalcogen bases do not possess adjacent lone-pair electrons. The influence of the halide leaving groups on the α-effect and the origin of the α-effect in the E2 reactions of ethyl halides are investigated and discussed.

1. Introduction

The term "α-effect" refers to the abnormal increased reactivity exhibited by nucleophiles (Nu) possessing one or more nonbonding electron pairs at the atom adjacent to the nucleophilic site (these nucleophiles are denoted as α-Nu). The α-effect has been experimentally and theoretically studied

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for more than 40 years.[1−7] It was first observed by Jencks and Carriuolo in 1960 in a series of chemical kinetics experiments involving the reaction of the ester *p*-nitrophenyl acetate with a range of nucleophiles.[1a] In 1962, Edwards and Pearson introduced the term α-effect for this anomaly.[1b] Over the years, many theories have been put forward to rationalize this effect, including (1) transition state (TS) stabilization arising from the favorable interaction between an adjacent lone pair and the partial positively charged reaction center in the carbocation;[2] (2) destabilization of the ground state (GS) due to electronic repulsion between the α lone-pair and the nucleophilic electron pair, thereby making the species more reactive;[3] (3) different solvent effects for regular and α-Nu;[4] and (4) thermodynamic stability of the product.[5] However, the true origin of α-effect is still not yet completely understood. There is also the question of whether the α-effect exists in the gas phase. Some experimental and theoretical studies suggest that the α-effect is not manifested in the gas phase, i.e., it arises from solvent effect,[6] while other studies indicate that the α-effect is present in gas-phase reactions.[7] In recent papers, we have made extensive theoretical studies and provided the evidence of the α-effect in gas-phase S_N2 and E2 reactions,[7d−g] where the magnitude of α-effect was evaluated by the downward deviation from the plot of overall enthalpy of activation, $\Delta H^{\ddagger}$, with respect to separated reactants vs proton affinity (PA) of regular Nu (or base). Recently, Villano et al.[6c] pointed out that the entropic effect should also be considered because it would influence the reactivity of nucleophiles. According to transition-state theory, the reaction rate constant k is calculated by $(k_B T/h)\exp(-\Delta G^{\ddagger}/RT)$. Hence, it is more appropriate to evaluate the E2 and S_N2 reactivity of various Nu's or bases using overall Gibbs free energy of activation, $\Delta G^{\ddagger}$. Correspondingly, the gas basicity (GB) is measured by the negative of the Gibbs free energy change associated with the reaction $A^- + H^+ \rightarrow HA$.

Here, we investigate the α-effect in E2 reactions using the relationship between $\Delta G^{\ddagger}$ and GB. First, a series of anionic E2 reactions toward ethyl chloride with 12 bases having the general structure H_nX^- where X belongs to the groups 14−17 elements of the periodic table (X = F, Cl, Br, O, S, Se, N, P, As, C, Si, and Ge) are reinvestigated (eq 1), and the corresponding competitive S_N2 reactions (eq 2) are also discussed for comparison. The model reactions for exploring the α-effect in E2 include the reactions of CH_3CH_2Cl with five regular bases, HO^-, HS^-, HSe^-, CH_3O^-, and $CH_3CH_2O^-$; five prototypic α-oxybases with adjacent lone pair electrons, YO^- (Y = F, Cl, Br, HO, and HS) (eq 3, X = Cl); six chalcogen bases with an adjacent triple bond, $RC{\equiv}CZ^-$ (R = H and Cl; Z = O, S, and Se) (eq 5), and carboanion $HC{\equiv}C^-$ (eq 1, A = HC≡C). Finally, we will study the influence of the halide leaving groups on the α-effect in the E2 and S_N2 reactions of CH_3CH_2X (X = F, Cl, and Br) with five α-oxybases (eqs 3 and 4).

$$A^- + CH_3CH_2Cl \rightarrow CH_2{=}CH_2 + HA + Cl^- \qquad (1)$$

$$A^- + CH_3CH_2Cl \rightarrow CH_3CH_2A + Cl^- \qquad (2)$$

$$(A = F, Cl, Br, HO, SH, SeH, NH_2, PH_2, AsH_2, CH_3, SiH_3, GeH_3, CH_3O, CH_3CH_2O, HC{\equiv}C)$$

$$YO^- + CH_3CH_2X \rightarrow CH_2{=}CH_2 + HOY + X^- \qquad (3)$$

$$YO^- + CH_3CH_2X \rightarrow CH_3CH_2OY + X^- \qquad (4)$$

$$(Y = F, Cl, Br, HO, \text{and } HS; X = F, Cl, \text{and } Br)$$

$$RC{\equiv}CZ^- + CH_3CH_2Cl \rightarrow CH_2{=}CH_2 + RC{\equiv}CZH + Cl^- \qquad (5)$$

$$(R = H \text{ and } Cl; Z = O, S, \text{and } Se)$$

The main objectives of this paper include the following: to examine the reactivity of various Nu's and bases in the gas-phase base-induced E2 and S_N2 reactions; to analyze the influence of leaving group on the magnitude of α-effect in E2 and S_N2 reactions; and to explore the origin of the α-effect by carrying out activation strain analyses. We hope the present study will lead to a better understanding of the α-effect in the gas phase and will also be useful for experimental studies in the future.

2. Calculation Methods

It has been shown that the G2(+) theory, introduced by Radom et al.,[8a] affords a good description for anionic S_N2 and E2 reactions.[7d−g,8a−d] Therefore, we here continued to use this method. It is noted that the original G2(+) procedure corrects the zero-point vibrational energy (ZPVE) using the scaled (by a factor of 0.8929) HF/6-31+G(d) frequencies. For some of the E2 TSs found in this work, the structures optimized at the HF/6-31+G(d) level are considerably different from those obtained at MP2(fc)/6-31+G(d). For example, the eclipsed E2 TS $[YO\cdots H\cdots CH_2CH_2\cdots Cl]^{-\ddagger}$ (Y = F and Cl) found at the HF level becomes moderately gauche [$Y{-}O{-}C_{\beta}{-}C_{\alpha} = 46.8°$ (Y = F) or 34.7° (Y = Cl)] at MP2(fc)/6-31+G(d). Accordingly, all minima and TSs were characterized with analytical second derivatives at MP2(fc)/6-31+G(d), and a scaling factor of 0.98 was applied to the ZPVE corrections.[9] Charges were calculated by the natural population analysis (NPA)[10] at the MP2(fc)/6-311+G(3df,2p) level on the MP2(fc)/6-31+G(d) geometries. All calculations were performed with the GAUSSIAN 03 suite of programs.[11] Throughout this paper, relative energies (in kJ mol^{-1}) refer to the Gibbs free energy changes, ΔG, at 298 K. All MP2(fc)/6-31+G(d)-optimized geometries and NPA charges are provided in the Supporting Information.

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TABLE 1. G2(+) Gas-Phase Basicities (GBs) of Anions, Overall Gibbs Free Energies of Activation, $\Delta G^{\ddagger}$(E2), Deformation Energies, ΔG_{def}(E2), and Interaction Energies, ΔG_{int}(E2) between the Deformed Reactants in the TSs for the Gas-Phase E2 Reactions of CH_3CH_2Cl with Regular Bases, α-Oxybases, and Pseudo-α-bases[a]

anions	GB[b]	$\Delta G^{\ddagger}$(E2)	ΔG_{def} (E2)	ΔG_{int} (E2)	$\Delta G^{\ddagger}$(S_N2)	ΔG_{def} (S_N2)	ΔG_{int} (S_N2)
F^-	1526.7	−32.3	144.7	−177.0	−21.3	84.2	−105.5
Cl^-	1375.1	87.2	257.1	−169.9	43.7	133.7	−90.0
Br^-	1332.6	118.2	311.3	−193.1	63.8	141.2	−77.4
HO^-	1605.6	−31.5	88.4	−119.9	−20.7	66.0	−86.7
HS^-	1447.9	76.4	201.2	−124.8	33.7	99.5	−65.8
HSe^-	1402.7	102.6	235.3	−132.7	53.6	97.7	−44.1
NH_2^-	1660.1	−17.8	107.4	−125.2	−12.7	50.0	−62.6
PH_2^-	1507.4	68.7	156.7	−88.0	30.9	75.3	−44.4
AsH_2^-	1469.0	86.4	180.9	−94.5	44.1	68.8	−24.7
CH_3^-	1712.0	−4.4	55.4	−59.8	−7.1	35.9	−42.9
SiH_3^-	1528.2	81.6	161.6	−80.0	41.3	77.4	−36.0
GeH_3^-	1483.0	95.1	191.3	−96.2	57.1	89.1	−32.1
$HC{\equiv}C^-$	1547.6	43.1	130.1	−87.0	29.2	84.2	−55.0
CH_3O^-	1568.0	−12.4	102.9	−115.3	−12.5	72.3	−84.8
$CH_3CH_2O^-$	1553.1	−2.1	110.7	−112.8	−2.2	78.2	−80.4
FO^-	1482.4	10.2	148.1	−137.9	−3.1	72.9	−75.9
ClO^-	1464.3	21.0	148.6	−127.6	7.2	79.1	−71.9
BrO^-	1462.7	27.9	153.2	−125.3	15.6	84.5	−68.9
HOO^-	1542.2	−14.4	114.9	−129.3	−18.5	56.9	−75.5
HSO^-	1469.5	29.1	147.9	−118.8	15.5	82.0	−66.5
CH_3OO^-	1528.0	0.6	122.1	−121.5	−6.7	73.1	−79.9
$HC{\equiv}CO^-$	1359.7	98.0	228.6	−130.6	70.0	132.9	−62.9
$HC{\equiv}CS^-$	1358.9	121.0	288.0	−167.0			
$HC{\equiv}CSe^-$	1342.5	130.2	296.5	−166.3			
$ClC{\equiv}CO^-$	1330.0	121.0	252.0	−131.0			
$ClC{\equiv}CS^-$	1344.3	129.2	311.3	−182.0			
$ClC{\equiv}CSe^-$	1323.1	144.1	310.4	−166.3			

[a] Selective $\Delta G^{\ddagger}$(S_N2), ΔG_{def} (S_N2), and ΔG_{int} (S_N2) are also listed for comparison. All energies are in kJ mol^{-1}. [b] The available experimental gas basicities (GBs, kJ mol^{-1}) of anions are taken from ref 12: F^- (1529.3 ± 0.84); Cl^- (1372.8 ± 0.4); Br^-(1331.8 ± 0.8); HO^- (1605.4 ± 1.3); HS^- (1441.0 ± 13); HSe^- (1402.5 ± 3.3); NH_2^- (1656.9 ± 0.8); PH_2^- (1520.0 ± 8.4); AsH_2^-(1464.0 ± 8.4); CH_3^- (1709.6 ± 3.3); SiH_3^- (1530.0 ± 8.4); GeH_3^-(1467.0 ± 8.4); CH_3O^-(1569.0 ± 4.6); $CH_3CH_2O^-$ (1555.0 ± 4.6); $HC{\equiv}C^-$(1550.0 ± 20.0); FO^- (1490.0 ± 15.0); ClO^-(1461.0 ± 5.0); BrO^-(1452. ± 11.0); HOO^- (1546.0 ± 1.7); CH_3OO^- (1538.0 ± 2.9);

3. Results and Discussion

The G2(+) GBs are listed in Table 1, showing that the calculated results are in good agreement with the available experimental data.[12]

3.1. Reactivity of Regular Anion in the Base-Induced E2 Reactions. In our previous study on the reactivity in the S_N2 and E2 reactions between CH_3CH_2Cl and regular anionic bases A^- (A = F, Cl, Br, HO, HS, HSe, NH_2, PH_2, AsH_2, CH_3, SiH_3, and GeH_3),[13] it was found that there is no general and straightforward relationship between $\Delta H^{\ddagger}$ and PA. Instead, discernible linear correlations exist only for the central atoms in A^- which belong to the same group of the periodic table. Similar correlations are also observed between $\Delta G^{\ddagger}$(E2) and GBs in the present work (see Figure 1) and also for S_N2 reactions, thus providing a good basis for the discussion of the S_N2 and E2 reactivity. These results suggest that it is more reasonable to make the reference line using the regular bases with the central atoms in the same group when discussing the α-effect in the S_N2 and E2 reactions.

The $\Delta G^{\ddagger}$(E2) sequence shows the following order of elimination reactivity toward CH_3CH_2Cl: $F^- > HO^- > NH_2^- > CH_3^- > PH_2^- > HS^- > SiH_3^- > AsH_2^- > Cl^- > GeH_3^- > HSe^- > Br^-$. Similarly, we can also get the following order for substitution reactivity: $F^- > HO^- > NH_2^- > CH_3^- > PH_2^- > HS^- > SiH_3^- > Cl^- > AsH_2^- > HSe^- > GeH_3^- > Br^-$. Both orders are slightly different from our previously reported sequences,[13] which were sorted with $\Delta H^{\ddagger}$(E2) and $\Delta H^{\ddagger}$(S_N2) values.

Inspection of the data in Table 1 shows that the differences of $\Delta G^{\ddagger}$(E2) values involving the regular bases of similar GB values could be considerable. Generally speaking, there will be higher reactivity for the base with a more electronegative attacking atom.[14] For example, the GB of F^- is 1.7 kJ mol^{-1} less than that of SiH_3^- (1526.7 vs 1528.4 kJ mol^{-1}, Table 1), but the $\Delta G^{\ddagger}$(E2) value of the former is lower than that of the latter by 113.9 kJ mol^{-1}, indicating the much stronger reactivity of F^- over SiH_3^- in E2 reactions. Moreover, sometimes a weaker base and a stronger base may exhibit similar reactivity, e.g., the GB of SiH_3^- is larger than those of AsH_2^- and Cl^- by 59.2 and 153.1 kJ mol^{-1}, respectively, but the E2 reactivities of all three bases toward CH_3CH_2Cl are very

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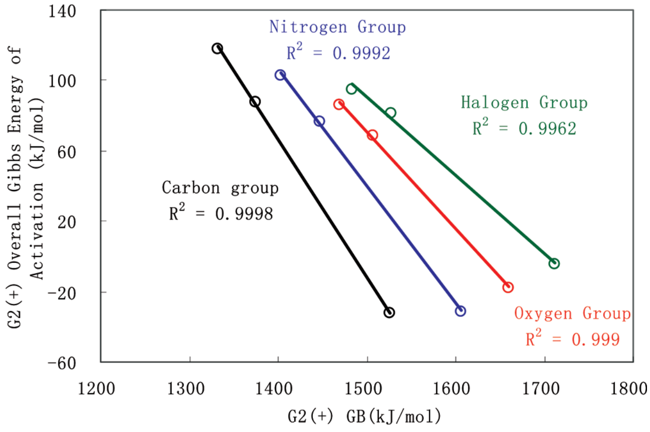

FIGURE 1. Plot of the G2(+) overall free energy of activation vs the GB (both in kJ mol^{-1}) for the E2 reactions of ethyl chloride with 12 regular bases H_nX^- (X = F, Cl, Br, O, S, Se, N, P, As, C, Si, and Ge).

similar [$\Delta G^{\ddagger}$(E2), in kJ mol^{-1}, is 81.6 for SiH_3^-, 86.4 for AsH_2^-, and 87.2 for Cl^-, Table 1]. These results indicate that, in addition to GB, the electronegativity (EN) of the central atom of the base is also an important factor for the reactivity in the E2 reaction.[14,15] A two-parameter equation, eq 6, can be derived to connect $\Delta G^{\ddagger}$(E2) with the combination of GB and EN values of the attacking site, where the EN values are calculated using eq 7, as proposed by Luo and Benson[16] where n is the number of valence electrons and r is the covalent radius in Ångstrom[17] for the attacking atom of the regular base. Equation 6 can be used to predict the approximate reactivity of a regular base toward CH_3CH_2Cl based on only the GB and EN values of the base's central atom.

$$\Delta G^{\ddagger}(\mathrm{E2}) = -0.38\mathrm{GB} - 17.07\mathrm{EN} + 717.86\ (R^2 = 0.986, N = 12) \qquad (6)$$

$$\mathrm{EN} = n/r \qquad (7)$$

3.2. Existence of α-Effect in Gas-Phase E2 Reactions. Experimental determination of the α-effect has often been carried out by comparing structurally similar nucleophiles, e.g., HOO^- vs HO^-[1a,4d] or ^{t}BuOO$^-$ vs ^{t}BuO$^-$,[1c] etc. However, numerous studies[14,15,18] of both the E2 and S_N2 reactions indicate that reactivity depends strongly on the basicity of Nu or base, and the comparison of two Nu's or bases with significantly different GB values may be misleading. Our calculations show that in the reaction with CH_3CH_2Cl, the $\Delta G^{\ddagger}(S_N2)$ value for a stronger base HO^- is still lower than that of HOO^- by 2.2 kJ mol^{-1}, in contrast to previous reported $\Delta H^{\ddagger}(S_N2)$ results,[7f] where the value of $\Delta H^{\ddagger}(S_N2)$ for the reaction of CH_3CH_2Cl with HO^- is higher than that with HOO^- by 2.3 kJ mol^{-1}. The lower $\Delta G^{\ddagger}(S_N2)$ value for HO^- than HOO^- can be largely attributed to the higher GB of HO^- over that of HOO^- by more than 60 kJ mol^{-1} and the entropic effect. If the GB difference of two Nu's is less than 30 kJ mol^{-1}, e.g., GB(HOO^-) = 1542.2 vs GB(CH_3O^-) = 1568.0 kJ mol^{-1}, or GB($CH_3CH_2O^-$) = 1553.1 vs GB(CH_3OO^-) = 1528.0 kJ mol^{-1}, the $\Delta G^{\ddagger}(S_N2)$ values for the reactions of CH_3CH_2Cl with α-Nu's (HOO^- or CH_3OO^-) are still lower than those of regular Nu's (CH_3O^- or $CH_3CH_2O^-$) by 6.0 or 4.5 kJ mol^{-1}, respectively, indicating that there is α-effect in gas-phase reactions; such a finding is consistent with the experimental and theoretical results by McAnoy et al.[7b] It should be noted that, in the DFT calculations by McAnoy et al., the S_N2(C) process with neutral dimethyl methylphosphonate (DMMP) has an overall activation energy 9.6 kJ mol^{-1} [$\Delta H^{\ddagger}$(0 K)] lower for HOO^- as compared to CH_3O^-, close to the corresponding value 8.3 kJ mol^{-1} in the present study. The barrier difference would be reduced to about 7.3 kJ mol^{-1} if enthalpy and entropy corrections are included and the leaving group difference [Cl^- vs $CH_3P(O)(OCH_3)O^-$] is neglected.

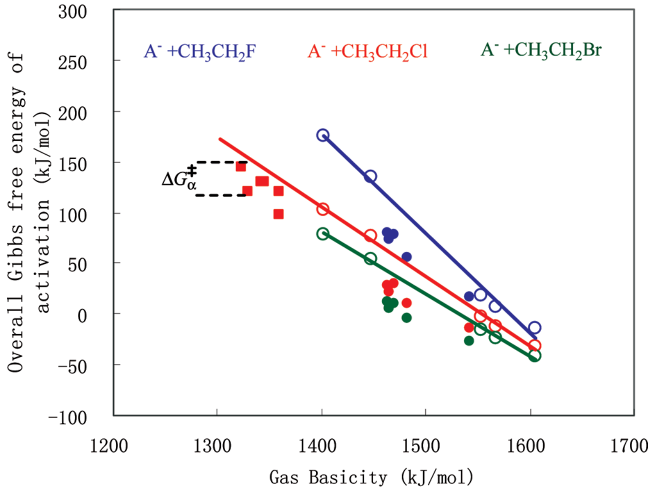

FIGURE 2. Plot of $\Delta G^{\ddagger}$(E2) vs GB of regular bases, HO^-, HS^-, HSe^-, CH_3O^-, and $CH_3CH_2O^-$ (open cycles), and α-base (filled cycles) for E2 reactions with CH_3CH_2F (blue), with CH_3CH_2Cl (red), and with CH_3CH_2Br (green). The red closed squares are for the E2 reactions of CH_3CH_2Cl with six pseudo-α-bases (left-to-right listing), $ClC{\equiv}CSe^-$, $ClC{\equiv}CO^-$, $HC{\equiv}CSe^-$, $ClC{\equiv}CS^-$, $HC{\equiv}CS^-$, and $HC{\equiv}CO^-$.

The Brønsted-type plots shown in Figure 2 exhibit a good linear ($R^2 > 0.99$) relationship between $\Delta G^{\ddagger}$(E2) and GB for the E2 reactions of ethyl halides with five regular bases, HO^-, HS^-, HSe^-, CH_3O^-, and $CH_3CH_2O^-$, with the attacking atoms in the same group of the periodic table. However, there are exceptions for five α-oxybases, FO^-, ClO^-, BrO^-, HOO^-, and HSO^-, which exhibit obvious downward deviation from the Brønsted-type plots (i.e., α-effect, see closed circles in Figure 2). An examination of the data in Table 2 reveals that the $\Delta G_\alpha^{\ddagger}$(E2) values increase as the leaving groups' basicities decrease, analogous to the previously reported trend for the S_N2 reactions with methyl halides.[7e] Moreover, $\Delta G_\alpha^{\ddagger}$(E2) values are usually larger than the corresponding $\Delta G_\alpha^{\ddagger}(S_N2)$ ones because E2 reactions are more sensitive to the GB values with a larger slope for the correlation line.

The structural features of these E2 TSs for the reactions of ethyl halides with α-base indicate that the favorable interaction between the electron-rich α-atom and the electron-deficient $C_\alpha - C_\beta$ π orbital in E2 TS is an important factor inducing the α-effect of E2 reactions (see Figure 3). Therefore, we can postulate that if the attacking site of base is adjacent to an electron-rich multiple bond such as a C≡C triple

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TABLE 2. **Magnitude of α-Effect, $\Delta G^{\ddagger}{}_{\alpha}$(E2) (in kJ mol^{-1}), for E2 Reactions of CH_3CH_2X (X = F in Bold Font, X = Cl in Normal Font, and X = Br in Italic Font) with Five α-bases, YO^- (Y = F, Cl, Br, HO, and HS)[a]**

anions	$\Delta G_{\alpha}{}^{\ddagger}$(E2-F)	$\Delta G_{\alpha}{}^{\ddagger}$(E2-Cl)	$\Delta G_{\alpha}{}^{\ddagger}$(E2-Br)
FO^-	**41.1 (32.0)**	39.1 (25.7)	*34.8 (23.8)*
ClO^-	**42.3 (26.0)**	40.7 (22.2)	*36.9 (19.9)*
BrO^-	**36.9 (17.6)**	34.9 (14.3)	*31.3 (12.4)*
HOO^-	**21.4 (24.1)**	22.6 (19.1)	*20.2 (18.4)*
HSO^-	**31.4 (14.5)**	29.0 (11.9)	*27.8 (10.5)*

[a] The $\Delta G_{\alpha}{}^{\ddagger}(S_N2)$ values are also listed in parentheses for comparison.

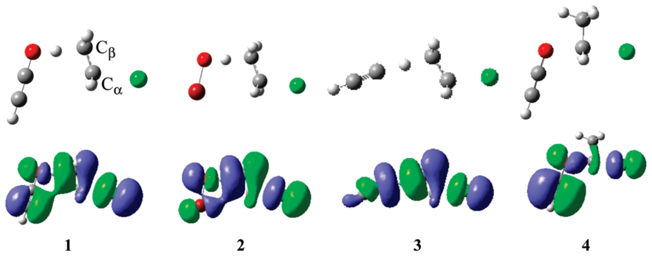

FIGURE 3. Pictorial representation of HOMOs for the E2 TSs of CH_3CH_2Cl with $HCCO^-$ (**1**), BrO^- (**2**), and $HC{\equiv}C^-$ (**3**). The last one on the right (**4**) is the S_N2 TS of $CH_3CH_2Cl + HCCO^-$.

bond instead of lone pair, an enhanced reactivity is likely to be observed, which is confirmed by our G2(+) calculations. As illustrated in Figure 2, the $\Delta G^{\ddagger}$(E2) values for the two oxybases without adjacent lone-pair electrons, such as $RC{\equiv}CO^-$ (R = H and Cl), marked by red closed square, are obviously smaller than the predicted ones by the Brønsted-type linear correlation, indicating that these oxyanions also display properties analogous to those prototypic α-bases. Hence, analogous to the name pseudohalogen, the term pseudo-α-base is proposed for these bases in order to differentiate them from α-bases bearing α lone pairs. These pseudo-α-bases exhibit moderate α-effect with $\Delta G^{\ddagger}{}_{\alpha}$(E2) about 34 kJ mol^{-1}, but the effect is not observed in the corresponding S_N2 reactions. The $\Delta G^{\ddagger}(S_N2)$ value for the reaction of CH_3CH_2Cl with $HC{\equiv}CO^-$ is 70 kJ mol^{-1}, even slightly higher than the predicted one by 2 kJ mol^{-1} (see Table 3), due to the disappearance of donor–acceptor interaction between the C≡C triple bond with electron-deficient $C_\alpha-C_\beta$ π orbital in S_N2 TS (see **4** in Figure 3). A decrease of the electron density on the C≡C moiety will lead to a weaker α-effect, which is supported by the NPA charge distributions in TSs, $[RC{\equiv}CO\cdots H_\beta\cdots CH_2CH_2\cdots Cl]^{-\neq}$ (R = H and Cl), presented in Table S1, Supporting Information. If the attacking atom in the pseudo-α-base is another chalcogen atom, such as sulfur and selenium, the $\Delta G^{\ddagger}{}_{\alpha}$(E2) values for the E2 TSs $[RC{\equiv}CZ\cdots H_\beta\cdots CH_2CH_2\cdots Cl]^{-\ddagger}$ (R = H and Cl; Z = S and Se) become smaller. This can be explained by the much lower EN values of sulfur and selenium and higher deformation energies for the E2 TSs with $RC{\equiv}CZ^-$ (R = H and Cl; Z = S and Se), whereas the analogous EN values for sulfur and selenium would lead to their similar $\Delta G^{\ddagger}{}_{\alpha}$(E2) values (see Table 3).

Interestingly, the $\Delta G^{\ddagger}$(E2) value for $HC{\equiv}C^-$ toward CH_3CH_2Cl is found to be significantly lower than the one predicted by the Brønsted-type plot of three carbon-group bases ($CH_3{}^-$, $SiH_3{}^-$, and $GeH_3{}^-$) by 26.3 kJ mol^{-1}, whereas the $\Delta G^{\ddagger}(S_N2)$ value for $HC{\equiv}C^-$ is smaller than the predicted one by 8.6 kJ mol^{-1}. This could be attributed to the higher EN value of the attacking sp carbon atom than a sp^3 carbon atom.

TABLE 3. **Magnitude of α-Effect, $\Delta G^{\ddagger}{}_{\alpha}$(E2) (in kJ mol^{-1}), for E2 Reactions of CH_3CH_2Cl with Six Pseudo-α-bases, $RC{\equiv}CZ^-$ (R = H and Cl; Z = O, S, and Se), and the $\Delta G_{\alpha}{}^{\ddagger}(S_N2)$ for $HC{\equiv}CO^-$ Is Given in Parentheses As Comparison**

R = H, Z = O, S, Se	$\Delta G^{\ddagger}{}_{\alpha}$(E2)	R = Cl, Z = O, S, Se	$\Delta G^{\ddagger}{}_{\alpha}$(E2)
$HC{\equiv}CO^-$	35.5 (−2.0)	$ClC{\equiv}CO^-$	32.8
$HC{\equiv}CS^-$	13.0	$ClC{\equiv}CS^-$	14.8
$HC{\equiv}CSe^-$	15.0	$ClC{\equiv}CSe^-$	14.5

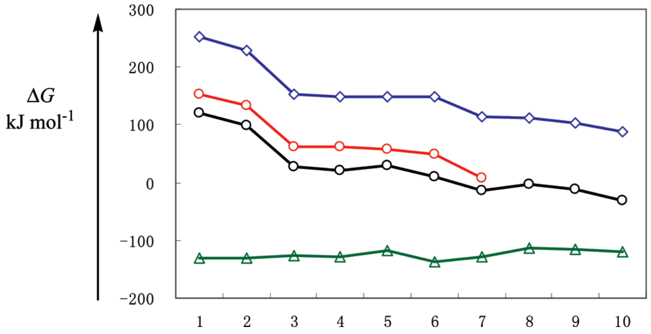

FIGURE 4. Variations of base with deformation energy (blue line), interaction energy between the deformed reactants (green line), G2(+) overall free energy of activation (black line), and the predicted overall free energy of activation by Brønsted-type correlation (red line) for the E2 reactions of ethyl chloride with oxybases along the increasing GB ((1) $ClC{\equiv}CO^-$; (2) $HC{\equiv}CO^-$; (3) BrO^-; (4) ClO^-; (5) HSO^-; (6) FO^-; (7) HOO^-; (8) $CH_3CH_2O^-$; (9) CH_3O^-; and (10) HO^-).

3.3. Exploring the Origin of the α-Effect by Activation Strain Analyses. In order to shed further light to the origin of α-effect in E2 reactions, we apply the activation strain model of chemical reactivity[19] to analyze the factors that control the barrier heights of E2 reactions. In this model, $\Delta G^{\ddagger}$ would be partitioned into deformation energy, ΔG_{def}, and interaction energy, ΔG_{int}, between the deformed reactants in the E2 TS. Figure 4 illustrates the variations of ΔG_{def}(E2), ΔG_{int}(E2), and their sum, $\Delta G^{\ddagger}$(E2), for a series of E2 reactions with oxybases along increasing GB values.

Generally speaking, the ΔG_{def}(E2) value is larger for a weaker base involved in the base-induced E2 reactions since the TS is formed at a relatively late stage. It was also found that all of the ΔG_{def}(E2) values are significantly larger than the corresponding $\Delta G_{def}(S_N2)$ ones, indicating that the E2 TSs are highly disordered and entropically favorable compared to the S_N2 TSs, as pointed out by Brauman et al.[20] The larger deformation energy will destabilize the TS and raise the overall barrier, but when the interaction between the deformed reactants is stronger, the activation barrier, $\Delta G^{\ddagger}$, will be lower than the predicted one. For example, the ΔG_{def} value for the E2 TS with a pseudo-α-base, $HC{\equiv}CO^-$, is much larger than that for α-base, BrO^-, due to its weaker basicity [GB(BrO^-) = 1462.7 kJ mol^{-1} vs GB($HC{\equiv}CO^-$) = 1359.7 kJ mol^{-1}]. Meanwhile, the ΔG_{int} value for the former is lower than that for the latter TS by 5.3 kJ mol^{-1}, thus

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leading to similar $\Delta G^{\ddagger}{}_{\alpha}$(E2) values (35.5 vs 34.9 kJ mol^{-1}, Table 2).

For the gas-phase S_N2 reactions, the variation of deformation energies is somewhat different from that for E2 reactions. The $\Delta G_{def}(S_N2)$ values for some α-Nu's with weaker basicity may be lower than those for regular bases with higher GB values, reflecting the characteristic of tight TS structures for those α-Nu's. Even though HOO$^-$ is an Nu with weaker basicity [GB(HOO$^-$) = 1542.2 kJ mol^{-1}], the deformation energy for S_N2 TS, $[HOO\cdots CH_3CH_2\cdots Cl]^{-\ddagger}$, is still lower than that for the regular stronger base, CH_3O^-, [GB(CH_3O^-) = 1568.0 kJ mol^{-1}], by about 15 kJ mol^{-1}. Meanwhile, the interaction energy between deformed reactants for the former S_N2 TS is only weaker than that of latter by 9.3 kJ mol^{-1}, leading to a lower activation barrier for α-Nu, HOO$^-$. This situation is also observed for the comparison between α-Nu, CH_3OO^- [GB(CH_3OO^-) = 1528.0 kJ mol^{-1}] and regular base $CH_3CH_2O^-$ [GB($CH_3CH_2O^-$) = 1553.1 kJ mol^{-1}].

As in the case of E2 reactions, $\Delta G_{int}(S_N2)$ is also responsible for the magnitude of α-effect, and stronger interaction between the deformed reactants will induce a higher $\Delta G^{\ddagger}{}_{\alpha}(S_N2)$ value (see Table 2). For example, in the S_N2 reaction of CH_3CH_2X (X = F, Cl, and Br) with FO$^-$, the increment of $\Delta G^{\ddagger}{}_{\alpha}(S_N2)$ values from X = Br to X = F can be rationalized by the increasing interaction between a neighboring fluorine atom with a higher electron density and an increasing positively charged reaction center (C_α) from bromine to fluorine (since the latter is a poor leaving group). That rationalization can be also applied for the corresponding E2 reactions. All of these results indicate that, even though there is a fairly good correlation between ΔG_{def} with $\Delta G^{\ddagger}$, the magnitude of α-effect in E2 and S_N2 will be determined by both of ΔG_{def} and ΔG_{int}.

4. Concluding Remarks

We have studied base-induced E2 reactions between ethyl chloride and a series of regular, α-, and pseudo-α-bases and developed a correlation between $\Delta G^{\ddagger}$(E2) with the GB and EN values of the attacking site for a series regular bases. Our results demonstrate the existence of α-effect in the gas-phase E2 reactions not only with α-bases but also with pseudo-α-bases. The E2 TS having the eclipsed conformation for the reactions with pseudo-α-bases suggests that the favorable orbital interaction is the major factor to induce α-effect. This result supports the idea that α-effect arises from TS stabilization. These conclusions are further confirmed by the enhanced α-effect as the basicity of the leaving group increases. It must be stressed that the existence of α-effect in the gas phase does not imply that the solvent effect is unimportant. In fact, the experimental S_N2 reaction rate ratio in solvent, k_{HOO^-}/k_{HO^-}, is usually larger than 50,[1b,4d] corresponding to a Gibbs activation free energy difference of about more than 10 kJ mol^{-1}, revealing that the α-effect in solvent is more important than that in the absence of solvent. This can be proved by the calculations that take solvent effect into account. Applying the IEFPCM model,[21] the overall Gibbs free energy of activation, $\Delta G^{\ddagger}(S_N2)$, in DMSO for the S_N2 reaction of CH_3CH_2Cl with HOO$^-$ is 80.4 kJ mol^{-1} at G2(+)-IEFPCM(MP2/6-31+G(d)), lower than that with HO$^-$ by 9.8 kJ mol^{-1}, indicating the presence of an enhanced α-effect in solvent.

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Supporting Information Available: MP2(fc)/6-31+G(d) optimized geometries and NPA charges for all E2 TS structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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