

## Substituent Effects on the Gas-Phase Pyrolyses of 2-Substituted Ethyl *N,N*-Dialkylcarbamates: A Theoretical Study

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The R- and Z-substituent effects for the gas-phase thermal decompositions of carbamates,  $R_2NC(=O)OCH_2CH_2Z$ , have been investigated theoretically at B3LYP level with 6-31G(d) and 6-31++G(d,p) basis sets. Both the Z- and R-substituent effects on reactivity ( $\Delta H^\ddagger$ ) were well consistent with experimental results, although the R-substituent effect was underestimated theoretically. No correlations were found between activation enthalpies and reaction enthalpies. The substituent effects on reactivity seemed to be complicated at a glance, but were understandable by concurrent electronic and steric factors. Variations of bond lengths at TS structures were well correlated with the Taft's  $\sigma^*$  values and the TS structures became tighter as the Z-substituent became a stronger electron-acceptor ( $\delta\sigma^* > 0$ ). However the effects of R-substituents on the TS structures were much smaller when compared to those of Z-substituents.

**Key Words :** Pyrolysis of carbamates, Hybrid density functional method, Variation of TS structures, Linear free energy relationship

### Introduction

Thermal decomposition of 2-(Z)-substituted *N,N*-dialkylcarbamates has been known to produce an amine, an olefin and carbon dioxide through a stepwise mechanism shown in Chart 1<sup>1</sup> along with some important atom numbering. In a previous work,<sup>2</sup> we have investigated theoretically the gas-phase thermal decomposition of ethyl *N,N*-dimethylcarbamate ( $R = CH_3$  and  $Z = H$  in **I**) and found that the first step proceeds through a six-membered cyclic transition state (TS), **II**, and becomes a rate-limiting step due to entropy effects. The six-membered structures were generally accepted as genuine TS structures for thermal decompositions of acetates and carbonates,<sup>3</sup> and hence the thermal decompositions of carbamates might be similar to those of acetates and related compounds.

In thermal decompositions of 2-(Z)-substituted ethyl acetates,  $CH_3CO_2CH_2CH_2Z$ , various substituent effects have

been used to explain the reaction mechanism.<sup>4</sup> For example, electron-withdrawing Z-substituents showed a linear correlation with inductive parameters,  $\sigma_I$ , with a slope  $\rho_I = -1.03$  ( $r = 0.961$  at 400 °C), and alkyl and polar substituents separated by at least three methylene groups were correlated with Hancock's steric parameters,  $E_S^C$ ,<sup>5</sup> with slope  $\delta = -0.12$  ( $r = 0.916$  at 400 °C). Recently an interesting work on Z-substituent effects for 2-(Z)-substituted ethyl *N,N*-dimethylcarbamates,  $(CH_3)_2NCO_2CH_2CH_2Z$ , was reported.<sup>6</sup> However, for these carbamates, no good results were obtained using various linear free energy relationships. Only the application of the Taft  $\sigma^*$  values<sup>7</sup> gave three straight lines at the origin of  $\sigma^*(CH_3) = 0.0$ , (i) alkyl substituents with  $\rho^* = -1.94$  ( $r = 0.977$ ), (ii) electron-withdrawing polar substituents with  $\rho^* = -0.12$  ( $r = 0.936$ ), and (iii) multiple-bonded substituents or electron-withdrawing substituents interposed by a  $CH_2$  at the 2-position of the ethyl ester with  $\rho^* = +0.49$  ( $r = 0.991$ ). These results indicated that the

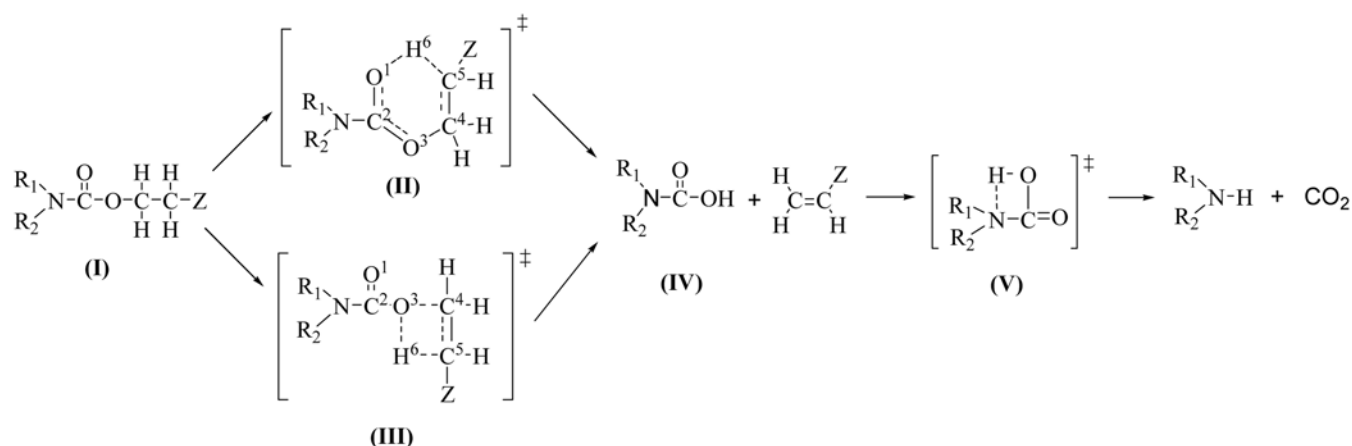


Chart 1

mechanistic criteria might be different although the common features of the TS structures seemed to be operative both in the cases of carbamates and acetates.

On the other hand, the rates of thermal decompositions were decreased as a bulky group, R, was substituted at the nitrogen atom of the carbamate.<sup>8</sup> For example, the replacement of two methyl groups on the nitrogen atom by phenyl groups resulted in a rate decrease by a factor of 10. This strongly implied that the steric factor had strong effect as suggested by experiments. However it has also been reported that the rate decreased for saturated heterocyclic carbamates but increased for unsaturated heterocyclic carbamates due to electronic factors.<sup>9</sup> Therefore it would be interesting to analyze both factors - steric and electronic factor, for the substituent effects on the nitrogen atom of the carbamates.

In this work, the substituent effects for thermal decompositions of the carbamates shown in Chart I were studied theoretically in order to elucidate the R- and Z-substituent effects on the reaction mechanism as a continuing work in our group on the theoretical elucidation of structures and reaction mechanism.<sup>10</sup>

### Calculations

In a previous theoretical work for the thermal decomposition of ethyl *N,N*-dimethyl carbamate,<sup>2</sup> the activation enthalpies ( $\Delta H^\ddagger$ ) calculated at B3LYP levels were consistent with the experimental values. Therefore we have studied thermal decomposition reactions by using the B3LYP level with 6-31G(d) and 6-31++G(d,p) basis sets in this work. Throughout this paper, B3LYP/6-31++G(d,p) results were used in the discussions unless noted otherwise.

All the stationary species were fully optimized and characterized by frequency calculations with all positive frequencies for reactants, intermediates and products and with only one imaginary frequency for transition states (TS).<sup>11</sup> The enthalpy changes ( $\Delta H$ ) at 633 K corresponding to the experimental temperature<sup>6</sup> were calculated by using eq. (1),<sup>12</sup> where  $\Delta E_{\text{ZPE}}$  and  $\Delta E_{\text{T}}$  are zero-point energy corrected electronic energy change at 0 K and thermal energy changes at 633 K, respectively. All the calculations were performed with the Gaussian 98 program package.<sup>13</sup>

$$\Delta H = \Delta E_{\text{ZPE}} + \Delta E_{\text{T}} + \Delta(\text{PV}) \quad (1)$$

### Results and Discussion

**(A) Z-substituent effects.** As mentioned above, it has been experimentally reported that the substituent effects for the thermal decompositions of **I** with R = CH<sub>3</sub> showed three distinct types of correlations with the Taft's  $\sigma^*$  values. Therefore three different types of Z-substituents were selected as a representative case for each type of a substituent: -C(CH<sub>3</sub>)<sub>3</sub> as an alkyl, -Cl as an electron-withdrawing and -C≡N as a multiple bonded substituent together with standard substituents CH<sub>3</sub> (for Taft equation) and H (for Hammett equation). The calculated activation enthalpies,

**Table 1.** Calculated and experimental activation enthalpies,  $\Delta H^\ddagger$ , and reaction enthalpies,  $\Delta H^0$  for the first step through the six-membered cyclic TS with R = CH<sub>3</sub> shown in Chart 1

| Z                                 | $\sigma^{*a}$ | $\Delta H^\ddagger^b$ |                | Exp. <sup>c</sup> | $\Delta H^0^b$ |
|-----------------------------------|---------------|-----------------------|----------------|-------------------|----------------|
|                                   |               | B3LYP/6-31G*          | B3LYP/6-31++G* |                   | B3LYP/6-31++G* |
| (CH <sub>3</sub> ) <sub>3</sub> C | -0.30         | 43.1                  | 39.7           | 40.5              | 7.0            |
| H <sub>3</sub> C                  | 0.00          | 45.0                  | 41.4           | 45.6              | 8.6            |
| H                                 | 0.49          | 44.6                  | 41.0           | 43.9              | 12.6           |
| Cl                                | 2.94          | 45.4                  | 42.0           | 46.1              | 10.3           |
| N≡C                               | 3.64          | 38.2                  | 34.9           | 36.7              | 9.1            |

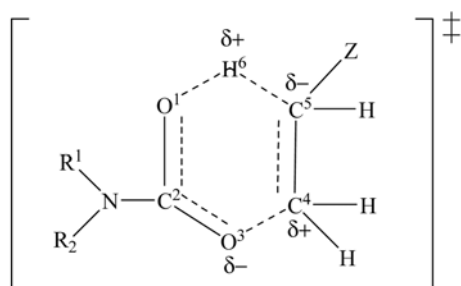
<sup>a</sup>Values are taken from Ref. 14. <sup>b</sup>Values are in kcal mol<sup>-1</sup> at 633 K. <sup>c</sup>Ref. 6

**Table 2.** The NPA of charge densities (q) and changes ( $\Delta q$ ) on going from **I** to **II** in electron unit at B3LYP/6-31++G(d,p) level

| Z                                 | I                  |        | II                               |                    | $\Delta q(\text{C}^5)$ | $\Delta q(\text{Z})$ |
|-----------------------------------|--------------------|--------|----------------------------------|--------------------|------------------------|----------------------|
|                                   | q(C <sup>5</sup> ) | q(Z)   | q <sup>‡</sup> (C <sup>5</sup> ) | q <sup>‡</sup> (Z) |                        |                      |
| (CH <sub>3</sub> ) <sub>3</sub> C | -0.488             | -0.008 | -0.587                           | 0.011              | -0.099                 | 0.019                |
| H <sub>3</sub> C                  | -0.485             | 0.014  | -0.602                           | 0.031              | -0.117                 | 0.017                |
| H                                 | -0.707             | 0.230  | -0.811                           | 0.248              | -0.104                 | 0.018                |
| Cl                                | -0.456             | -0.093 | -0.592                           | -0.075             | -0.136                 | 0.018                |
| N≡C                               | -0.594             | -0.043 | -0.727                           | -0.103             | -0.133                 | -0.060               |

$\Delta H^\ddagger$ , and reaction enthalpies,  $\Delta H^0$ , at 633 K for the first step through the six-membered cyclic TSs are collected in Table 1. Examination of Table 1 showed that the calculated  $\Delta H^\ddagger$  values at B3LYP/6-31G(d) level were slightly larger than those at B3LYP/6-31++G(d,p) level. However numerical differences between the calculated and experimental  $\Delta H^\ddagger$  values were as small as 0.7-4.1 kcal mol<sup>-1</sup> and the relative order of activation enthalpies of both theoretical levels were fully consistent with experimental results. Therefore it could be expected that the theoretical results are sufficiently reliable. Reaction enthalpies calculated at B3LYP/6-31++G(d,p) level showed no correlation with activation enthalpies.

To examine electronic effects of Z-substituents, changes in atomic charge densities on going from reactant to TS,  $\Delta q$ , were calculated by using the natural population analysis (NPA)<sup>14</sup> and collected in Table 2. As can be seen from Table 2, the atomic charge densities revealed an interesting phenomenon, *i.e.*, the charge density of a carbon center, q(C<sup>5</sup>), to which the Z-substituent is directly attached, became more negative as the reaction proceeded in all cases. These results are easily understandable - the hydrogen, which moves toward carbonyl oxygen, O<sup>1</sup>, seems to have proton character and hence charge density of C<sup>5</sup> at the TS increases as depicted in Scheme 1. Thus the Z-substituent effects on the reactivity,  $\Delta H^\ddagger$ , in terms of pure electronic effects, were generally expected to become more favorable (unfavorable) as an electron-withdrawing (-donating) ability increases. In fact, the  $\Delta H^\ddagger$  for Z = CN is the most favorable among reactions studied, since the electron accepting ability of CN ( $\sigma^* = 3.64$ ) is the largest. This is well agreed with the results of charge density analyses.



Scheme 1

However the relative order of  $\Delta H^\ddagger$  for  $Z=\text{Cl}$  ( $\sigma^* = 2.94$ ) or  $Z = (\text{CH}_3)_3\text{C}$  ( $\sigma^* = -0.30$ ) did not follow simple relationship between Taft's  $\sigma^*$ <sup>15</sup> and charge density analysis. In the case of  $Z=\text{Cl}$ ,  $\sigma^*$  value is larger than that of  $Z=\text{CH}_3$  ( $\sigma^* = 0.0$ ), which means that the activation barrier for the former should be lower than that of the latter. In fact the activation enthalpy for  $Z=\text{Cl}$  is the highest among the systems studied in this work. This strongly suggests that Cl should act as a relatively stronger electron donor than  $\text{CH}_3$  contrary to general belief. In a previous work,<sup>16</sup> we have reported the anomalous  $\pi$ -donating effects of  $\pi$ -accepting substituents in carbocationic systems and found that extent of  $\pi$ -donating effect is the largest for Cl substituent. Therefore, we believe that the lone pair orbitals on Cl act as a  $\pi$ -donor to a partially filled p-orbital on C. In order to determine the extent of electron donation from Cl, orbital interactions of interacting orbitals were deleted at B3LYP/6-31++G(d,p) level by using the natural bond orbital (NBO) analysis<sup>17</sup> and found that the extent of  $\pi$ -donating effect from lone-pair orbitals of Cl was 0.017e. This explains why the  $\Delta H^\ddagger$  for Cl is more unfavorable than for  $\text{CH}_3$ , even if the expected electron-accepting ability (based on  $\sigma^*$ ) is larger for Cl than for  $\text{CH}_3$ .

In the case of  $Z = (\text{CH}_3)_3\text{C}$ ,  $\Delta q(\text{C}^5)$  is the most negative due to the electron donating nature of *t*-butyl group ( $\sigma^* = -0.30$ ) but its activation energy is lower than that of  $Z=\text{CH}_3$ . Therefore, it might be expected that another effect played a more important role in the cases of  $Z = \text{alkyl}$  substituents. As is generally expected, steric congestion of *t*-butyl group on going from reactant to TS could be released, since the hybridization of  $\text{C}^5$  atom changed from  $\text{sp}^3$  to partial  $\text{sp}^2$  character as shown in Scheme 1. This implies that the steric effect is one of important factors influencing the reactivity in case of bulky substituent.

**(B) R-Substituent Effects.** It has been experimentally reported that the reactivity for thermal decomposition of ethyl *N,N*-diethylcarbamate ( $\text{R} = \text{CH}_3\text{CH}_2$ )<sup>1c</sup> was decreased slightly as compared to that of ethyl *N,N*-dimethylcarbamate ( $\text{R} = \text{CH}_3$ ).<sup>6</sup> These results have been explained by the stronger electron-donating ability of  $\text{R} = \text{CH}_3\text{CH}_2$  relative to  $\text{R} = \text{CH}_3$ . On the other hand, the reactivity was reduced when a bulky group with stronger electron-accepting ability such as a phenyl group was substituted at the nitrogen atom.<sup>8</sup> For example, the  $\Delta H^\ddagger$  at 653 K became larger by 5.4 kcal mol<sup>-1</sup> when  $\text{R}=\text{CH}_3$  was replaced by  $\text{R}=\text{Ph}$  group. Experimentally, it has been explained that the rate is decreased by

the concurrent steric effect in the case with  $\text{R} = \text{phenyl}$ .

The theoretical results obtained in this work were well consistent with the experimental results as summarized in Table 3. The  $\Delta H^\ddagger$  with  $\text{R} = \text{H}$  is favorable by 0.6 kcal mol<sup>-1</sup> than that with  $\text{R} = \text{CH}_3$ . The  $\Delta H^\ddagger$  is larger with bulky group,  $\text{R} = \text{phenyl}$  or *tert*-butyl group, when compared with  $\text{R} = \text{CH}_3$ .

Structurally, in  $\text{R} = \text{tert-butyl}$ , the dihedral angle between the carbonyl ( $\text{C}=\text{O}$ ) and the  $\text{NR}_1$  (or  $\text{NR}_2$ ) moiety deviated from planarity by 37.7° in the reactant due to steric congestions of two bulky *tert*-butyl substituent. Moreover such a distortion became more severe by 5.4° in the TS. Therefore the stabilizing conjugation effect between  $\pi^*(\text{C}=\text{O})$  orbital and a lone pair of N-atom is reduced. This could explain why the reactivity is reduced when *tert*-butyl group is substituted at the N atom.

However, such a dihedral angle distortion was not observed in  $\text{R} = \text{phenyl}$  because the deviation from planarity was less than 5° for both the reactant and TS. Moreover, bond angle,  $\angle \text{R}_1\text{NR}_2$ , in reactant or TS was almost same (Table 3). This indicated that the hybridization of N atom is little changed on going from the reactant to TS. Instead, two phenyl rings had to rotate from the  $\text{NC}(=\text{O})$  molecular plane in the reactant (41.1° and 68.3°) and became 54.1° and 54.6° in the TS. Deviations of phenyl rings from molecular plane could be clearly resulted from the steric congestion between two bulky phenyl groups, and thus the conjugation effects of the N lone pair might be influenced by these changes. As a result, the reactivity ( $\Delta H^\ddagger$ ) became less favorable for  $\text{R} = \text{phenyl}$  due to steric effects of bulky substituents. However,  $\Delta H^\ddagger$  difference between  $\text{R} = \text{C}_6\text{H}_5$  and  $\text{R} = \text{CH}_3$  calculated at 633 K is only 0.4 kcal mol<sup>-1</sup>, and this is much smaller than the difference observed experimentally. Therefore, theoretical results for R-substituent effects could be underestimated. Reaction enthalpies summarized in Table 3 showed no correlation with activation enthalpies similarly to that found for Z-substituent effects.

**(C) Substituent Effects on the TS Structures.** In order to examine TS structure variations, some important bond lengths in TS structures were collected in Table 4. Examination of Table 4 showed that both the bond lengths of  $d(\text{O}^1-\text{H}^6)$  and  $d(\text{O}^3-\text{C}^4)$  corresponding to bond formations and bond breakings, respectively, were shortened when the electron accepting abilities of Z-substituents (based on the

**Table 3.** Calculated and experimental activation enthalpies,  $\Delta H^\ddagger$ , reaction enthalpies,  $\Delta H^0$ , for the first step through the six-membered cyclic TS and bond angles,  $\angle \text{R}_1\text{NR}_2$ , at the reactant, **I**, and TS, **II**, for species with  $Z = \text{H}$  at B3LYP/6-31++G(d,p) level

| R                                 | $\sigma^*{}^a$ | $\Delta H^\ddagger{}^b$ | $\Delta H^0{}^b$ | $\angle \text{R}_1\text{NR}_2$ |           |
|-----------------------------------|----------------|-------------------------|------------------|--------------------------------|-----------|
|                                   |                |                         |                  | <b>I</b>                       | <b>II</b> |
| H                                 | 0.49           | 40.4                    | 21.1             | 119.2 °C                       | 119.5 °C  |
| H <sub>3</sub> C                  | 0.00           | 41.0                    | 12.6             | 116.5 °C                       | 117.1 °C  |
| (CH <sub>3</sub> ) <sub>3</sub> C | -0.30          | 41.6                    | 17.6             | 124.9 °C                       | 125.1 °C  |
| C <sub>6</sub> H <sub>5</sub>     | 0.60           | 41.4                    | 17.2             | 118.0 °C                       | 118.3 °C  |

<sup>a</sup> Values are taken from Ref. 14. <sup>b</sup> Values are in kcal mol<sup>-1</sup> at 633 K.

**Table 4.** The relevant bond lengths (in Å) in TS structures optimized at B3LYP/6-31++G(d,p) level

| R                                 | Z                                 | d(C <sup>5</sup> -H <sup>6</sup> ) | d(O <sup>1</sup> -H <sup>6</sup> ) | d(O <sup>3</sup> -C <sup>4</sup> ) |
|-----------------------------------|-----------------------------------|------------------------------------|------------------------------------|------------------------------------|
| CH <sub>3</sub>                   | (CH <sub>3</sub> ) <sub>3</sub> C | 1.306                              | 1.326                              | 2.025                              |
|                                   | H <sub>3</sub> C                  | 1.302                              | 1.326                              | 2.011                              |
|                                   | H                                 | 1.329                              | 1.288                              | 1.980                              |
|                                   | Cl                                | 1.386                              | 1.215                              | 1.906                              |
|                                   | N≡C                               | 1.502                              | 1.130                              | 1.748                              |
| H                                 |                                   | 1.325                              | 1.297                              | 1.999                              |
| (CH <sub>3</sub> ) <sub>3</sub> C | H                                 | 1.328                              | 1.293                              | 2.001                              |
| C <sub>6</sub> H <sub>5</sub>     |                                   | 1.335                              | 1.291                              | 2.023                              |

Taft's  $\sigma^*$  values) were increased. For example, d(O<sup>1</sup>-H<sup>6</sup>) and d(O<sup>3</sup>-C<sup>4</sup>) with Z = CN were much shorter by 0.196 Å and 0.277 Å, respectively, than those with Z = (CH<sub>3</sub>)<sub>3</sub>C. This indicates that the TS structure becomes tighter as the Z-substituent becomes a stronger electron-acceptor.

On the other hand, effects of the R-substituents on the TS structures were smaller than those of the Z-substituents. For example, d(O<sup>1</sup>-H<sup>6</sup>) bond length change between Z = H and Z = (CH<sub>3</sub>)<sub>3</sub>C was 0.038 Å, but d(O<sup>1</sup>-H<sup>6</sup>) bond length between R = H and R = (CH<sub>3</sub>)<sub>3</sub>C was only 0.004 Å. Such a small change in the bond lengths with R-substituents was caused by the concurrent electronic and steric effects as discussed above.

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