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Theoretical Studies on the Gas-Phase Pyrolysis of 2-Alkoxypyrimidines, 2-Alkoxypyrazines, 4-Ethoxypyrimidine and 3-Ethoxypyridazine[1]

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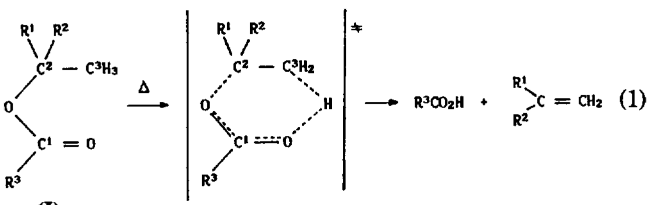
The gas-phase pyrolysis reactions of 2-alkoxypyrimidines(II), 2-alkoxypyrazines(III), 4-ethoxypyrimidine(IV) and 3-ethoxypyridazine(V) are investigated theoretically using the AM1 MO method. These compounds pyrolyze in a concerted retro-ene process with a six-membered cyclic transition state (TS). The relative order of reactivity is (IV)>(II)>(III)>(V), which can be rationalized by the two effects arising from electron-withdrawing power of the aza-substituent: (i) Electron withdrawal from the C-O bond accelerates the rate and (ii) electron withdrawal from the N^1-atom, that is participating in the six-membered TS, deactivates the reaction. We are unable to explain the experimental result of the greatest reactivity for pyridazine, (V), with our AM1 results. The reactivity increase accompanied by successive methylation of the ethoxy group, ethoxy<*iso*-propoxy>*tert*-butoxy, is due to a release of steric crowding in the activation process.

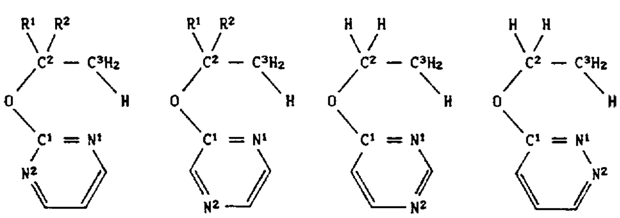
Introduction

Thermal decomposition of esters, (I), has been extensively studied experimentally[2] and theoretically[3], and it is believed to proceed by a concerted retro-ene type reaction with a six membered cyclic TS, Eq. (1). On the other hand, little work has been reported on the thermal decomposition of the nitrogen analogues of esters, imines and amides.



(I)

In a previous work[4], we examined theoretically the pyrolysis mechanism of 2-alkoxypyridines, and as part of a continuing effort to understand the pyrolysis mechanism we have carried out the AM1 studies of the pyrolysis reactivities of the aza-substituted pyridines, (II)~(V). The reactivity of these compounds has some interesting aspects: the aza-substituent exerts differing strength of inductive and resonance (or mesomeric) electron withdrawing effects (−I and −M) on the C^2-O bond and the N-atom participating in the six-membered cyclic TS (hereafter denoted as N^1) depending on the site in the ring. The effect of the aza-substitutent on the reactivity of thermal decomposition can be examined by comparing relative rates between these compounds, (II)-(V), and by relating the rates to that of the unsubstituted 2-alkoxypyridine.



(II) (III) (IV) (V)

The gas-phase experimental results of Al-Awadi *et al.*,[5] have shown an increase in the rate of decomposition due to methyl group substituted in the aromatic ring of 2-ethoxypyridine. The methyl group has dual effects: (i) Electron supply to the C^2-O bond hinders its cleavage and so decreases the reaction rate. (ii) Electron supply to the C=N bond raises the nucleophilicity of the nitrogen atom, thereby increasing the reaction rate. Of the two opposing effects, the latter is found to prevail experimentally. Moreover, the effect of a methyl group at the ortho- or para-position was greater than that at the meta-position. An aza-substituent, being an inductive electron-withdrawer, is expected to have exactly the opposite trend in the dual effects on the C^2-O and C=N bonds. However, the effect of the aza-substituent is more complex since the aza-substituent can also exert resonance (mesomeric) effect.

On the other hand, methyl group substituted on the alkoxy-alkyl group, *i.e.*, $R^1=R^2=Me$, are known to increase the reaction rate,[6] due probably to the two effects: (i) the electron supply to the C-atom stabilizes the positive charge developing in the TS. (ii) Bulky methyl groups accelerate the rate sterically.

In this work, we will examine these various effects of aza- and methyl-substituents on the pyrolysis rates of compounds (II)~(V) MO theoretically.

Computational Method

The AM1 procedure[7] was used throughout in this work. The ground states (geometries and energies) were fully optimized with respect to all geometrical parameters and characterized by all positive eigenvalues in the Hessian matrix.[8] TSs were located by the reaction coordinate method,[9] refined by the gradient norm minimization method,[10] and characterized by confirming onyl one negative eigenvalue in the Hessian matrix.[8] The activation entropy, ΔS^{*}, was obtained by substracting the calculated entropy of the ground state from that of the TS at 600 K, using a program incorporated within the AMPAC.[11]

Results and Discussion

The activation parameters, ΔH^{*}, ΔS^{*} and ΔG^{*}, and heats of reaction, ΔH_R, for the thermal decomposition processes of compounds (II)~(V) are presented in Table 1. Reference to this Table reveals that the reactivity increases with the successive methyl group substitution at the C^2-position, ($R^1=R^2=H$)<($R^1=H$, $R^2=Me$)<($R^1=R^2=Me$). This reactivity trend is consistent with that of the gas-phase experiments of Al-Awadi *et al.*,[12] and also with those of experimental and theoretical results for the 2-alkoxypyridines[4,5] and esters.[2,3] The acceleration of rate arising from the methyl substitution on the C^2-carbon, however, can not be attributed to the TS stabilization due to electron supply from the methyl group, since positive charge on the C^2-carbon, both in the GS and TS, increases with the methyl substitution, the increase being greater in the TS, as can be seen in Table 2. We suggest instead that the rate increase is ascribable to steric

Table 1. The AM1 Activation Parameters for The Thermal Decompositon Processes of the Compounds II-VI

Compound	Substituents	Activation parameters			ΔH_R[a]
		ΔH^{*b}	ΔS^{*c}	ΔG^{*d}	
II	$R^1=R^2=H$	55.0	−2.8	56.7	13.4
	$R^1=H$, $R^2=Me$	51.0	−1.8	52.7	6.0
	$R^1=R^2=Me$	46.9	+3.4	44.9	−1.3
III	$R^1=R^2=H$	57.3	−2.7	58.9	14.6
	$R^1=H$, $R^2=Me$	54.0	−1.6	55.0	7.5
	$R^1=R^2=Me$	49.8	+4.2	47.3	0.3
IV	$R^1=R^2=H$	56.1	−0.4	56.4	18.6
V	$R^1=R^2=H$	60.5	−0.6	60.7	14.5
IV[e]	$R^1=R^2=H$	56.5	−2.9	58.2	16.1

[a] $\Delta H_R=\Delta H_f$(Product complex)$-\Delta H_f$(Reactant) in kcal/mol. [b] $\Delta H^{*}=\Delta H_f$(TS)$-\Delta H_f$(Reactant) in kcal/mol. [c] $\Delta S^{*}=S$(TS)$-S$(Reactant) in cal/mol·degree at 600 K. [d] $\Delta G^{*}=\Delta H^{*}-T\Delta S^{*}$ in kcal/mol. [e] Reference 4.

Table 2. Charges (q) on The Heavy Atoms and H(C^3-H) for The Compounds II-VI of GS and TS in Electronic Charge Unit

Compound	Substituents		N^{TS}	C^1	O	C^2	C^3	H
II	$R^1=R^2=H$	GS	−0.217	+0.153	−0.174	−0.011	−0.246	+0.096
		TS	−0.273	+0.265	−0.329	+0.113	−0.590	+0.340
		Δq	−0.046	+0.112	−0.155	+0.124	−0.344	+0.244
	$R^1=H$, $R^2=Me$	GS	−0.226	+0.158	−0.178	+0.050	−0.240	+0.115
		TS	−0.309	+0.264	−0.377	+0.195	−0.537	+0.343
		Δq	−0.083	+0.106	−0.199	+0.145	−0.297	+0.228
	$R^1=R^2=Me$	GS	−0.229	+0.164	−0.182	+0.102	−0.236	+0.101
		TS	−0.372	+0.267	−0.467	+0.309	−0.447	+0.338
		Δq	−0.143	+0.103	−0.285	+0.207	−0.211	+0.237
III	$R^1=R^2=H$	GS	−0.175	+0.084	−0.200	−0.012	−0.246	+0.097
		TS	−0.229	+0.212	−0.334	+0.114	−0.593	+0.341
		Δq	−0.054	+0.128	−0.144	+0.126	−0.353	+0.244
	$R^1=H$, $R^2=Me$	GS	−0.175	+0.091	−0.203	+0.048	−0.240	+0.101
		TS	−0.268	+0.216	−0.393	+0.196	−0.549	+0.346
		Δq	−0.093	+0.125	−0.190	+0.148	−0.309	+0.245
	$R^1=R^2=Me$	GS	−0.177	+0.097	−0.205	+0.099	−0.235	+0.101
		TS	−0.345	+0.232	−0.490	+0.319	−0.466	+0.347
		Δq	−0.168	+0.135	−0.285	+0.220	−0.231	+0.246
IV	$R^1=R^2=H$	GS	−0.236	+0.159	−0.202	−0.012	−0.245	+0.098
		TS	−0.305	+0.297	−0.359	+0.144	−0.635	+0.359
		Δq	−0.069	+0.138	−0.157	+0.156	−0.390	+0.261
V	$R^1=R^2=H$	GS	−0.110	+0.068	−0.198	−0.012	−0.246	+0.104
		TS	−0.233	+0.227	−0.382	+0.135	−0.567	+0.364

		Δq	−0.123	+0.159	−0.184	+0.147	−0.321	+0.260
VI[a]	$R^1=R^2=H$	GS	−0.204	+0.129	−0.210	−0.009	−0.245	+0.096
		TS	−0.238	+0.261	−0.354	+0.117	−0.626	+0.342
		Δq	−0.034	+0.132	−0.144	+0.126	−0.380	+0.246

[a] Reference 4.

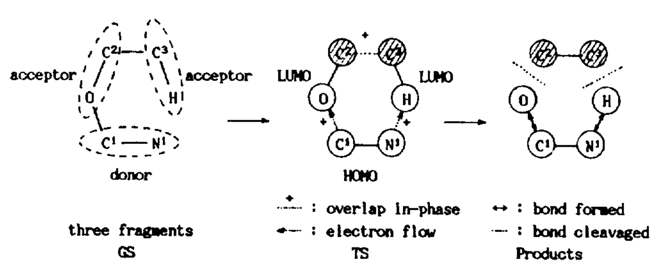
Table 3. Bond Lengths for The Compounds II-VI of GS and TS in Å

Compound	Substituents		N^{TS}-C^1	C^1-O	O-C^2	C^2-C^3	C^3-H	H-N
II	$R^1=R^2=H$	GS	1.377	1.378	1.436	1.508	1.116	2.717
		TS	1.401	1.304	1.738	1.405	1.534	1.156
		Δd	+0.024	−0.074	+0.302	−0.103	+0.418	−1.561
	$R^1=H$, $R^2=Me$	GS	1.375	1.375	1.440	1.514	1.115	2.649
		TS	1.399	1.300	1.865	1.414	1.412	1.253
		Δd	+0.024	−0.075	+0.425	−0.100	+0.297	−1.396
	$R^1=R^2=Me$	GS	1.376	1.372	1.454	1.519	1.114	2.577
		TS	1.401	1.288	2.126	1.480	1.275	1.463
		Δd	+0.025	−0.084	+0.672	−0.039	+0.161	−1.114
III	$R^1=R^2=H$	GS	1.359	1.373	1.437	1.508	1.116	2.712
		TS	1.379	1.301	1.738	1.405	1.546	1.152
		Δd	+0.020	−0.072	+0.301	−0.103	+0.430	−1.560
	$R^1=H$, $R^2=Me$	GS	1.357	1.370	1.440	1.513	1.116	2.638
		TS	1.378	1.297	1.861	1.414	1.424	1.243
		Δd	+0.021	−0.073	+0.421	−0.099	+0.308	−1.395
	$R^1=R^2=Me$	GS	1.357	1.368	1.452	1.519	1.115	2.597
		TS	1.378	1.287	2.113	1.424	1.284	1.444
		Δd	+0.021	−0.081	+0.661	−0.095	+0.169	−1.153
IV	$R^1=R^2=H$	GS	1.362	1.372	1.437	1.508	1.116	2.747
		TS	1.383	1.300	1.736	1.404	1.536	1.149
		Δd	+0.021	−0.072	+0.299	−0.104	+0.420	−1.598
V	$R^1=R^2=H$	GS	1.380	1.372	1.436	1.508	1.115	2.725
		TS	1.393	1.296	1.816	1.401	1.473	1.214
		Δd	+0.013	−0.076	+0.380	−0.107	+0.358	−1.511
VI[a]	$R^1=R^2=H$	GS	1.358	1.379	1.433	1.508	1.116	2.748
		TS	1.381	1.307	1.714	1.403	1.580	1.129
		Δd	+0.023	−0.072	+0.281	−0.105	+0.464	−1.619

[a] Reference 4.

effect of the bulky methyl group. In the GS, the C^2-carbon is sp^3-hybridized so that the methylation results in an increase in steric congestion, which can be relieved by stretching of the C^2-O bond (Table 3). This bond stretching causes a greater polarization of the C-O bond giving a greater positive charge on C^2 as noted above. In the TS, cleavage of the C^2-O bond takes place and renders the C^2-atom an intermediate hybrid ($sp^2 \sim sp^3$) character with a release of steric congestion and hence an increase in the rate. The steric releasing effect in the TS increases with successive methylation, and leads to a greater degree of C^2-O bond cleavage (Table 3) with a greater sp^2 character and positive charge (Table 2) of the C^2-atom.

In the framework of the frontier MO (FMO) theory,[13] the reactivity of the thermal decomposition of esters[3a] has been successfully interpreted by Fukui's three-species interaction[14] scheme (Scheme 1). We confirmed that the three FMO's in Scheme 1 indeed overlap in-phase as required by the theory. Examination of HOMO(C^1-N^1)-LUMO(O-C^2) energy gap listed in Table 4 indicates that the inter-frontier level gap decreases as the methyl group is substituted at C^2-position, which will favor the reactivity increase. Furthermore, the methyl substitution at C^2-position leads to a more stable product olefin, methyl substituted ethylenes, so that the enthalpy of reaction, ΔH_R, decreases, which is favorable for



Scheme 1.

Table 4. Ground State HOMO-LUMO Energy Levels for The Compounds II-III in eV

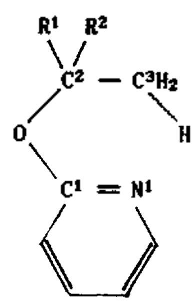
Compound	Substituents	ε_{HOMO} [a]	ε_{LUMO} (1) [b]	ε_{LUMO} (2) [c]	ε_{FMO} (1) [d]	ε_{FMO} (2)
II	$R^1=R^2=H$	−9.78	3.04	4.97	12.82	14.75
	$R^1=H$, $R^2=Me$	−9.72	3.05	5.02	12.77	14.74
	$R^1=R^2=Me$	−9.67	3.06	5.09	12.73	14.76
III	$R^1=R^2=H$	−9.51	3.04	4.92	12.55	14.43
	$R^1=H$, $R^2=Me$	−9.45	3.05	4.98	12.50	14.43
	$R^1=R^2=Me$	−9.41	3.06	5.02	12.47	14.43

[a] HOMO is a π-bonding orbital of $C^1=N^1$ bond. [b] LUMO is a σ^*-antibonding orbital of O-C^2 bond. [c] LUMO is a σ^*-antibonding orbital of C^3-H bond. [d] $\Delta\varepsilon_{FMO}(i)=\varepsilon_{LUMO}(i)-\varepsilon_{HOMO}$.

a greater reactivity thermodynamically.

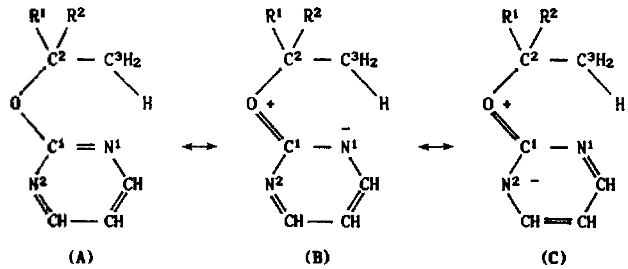
The reactivity order for the ethoxy species of (II)~(V) ($R^1=R^2=H$ for (II) and (III)) in Table 1 is (II)>(IV)>(III)>(V) based on the enthalpy of activation, ΔH^*, but the order changes to (IV)>(II)>(III)>(V) based on ΔG^* so that inclusion of the entropy of activation, ΔS^*, reverses the order between (II) and (IV). Thus ΔS^* plays an important role in determining the reactivity order of (II)~(V), due primarily to the small difference in ΔH^* ($\delta\Delta H^*\cong 1.1$ kcal/mol) between (II) and (IV)). In the following, we will discuss the effect of aza-substituent on the relative reactivity order for each individual compound.

2-Alkoxypirimidines, (II). The inductive electron withdrawing effect of the "substituent" nitrogen (hereafter denoted as N^2) is expected to decrease electron density (q) on the N^1-atm and lowers the nucleophilicity of N^1 toward the hydrogen on C^3-H and hence the reactivity of (II) is expected to be lower than that of pyridine, (VI). On the contrary, however, we note in Table 2 that $q(N^1)$ for (II) is actaually more negative ($q(N^1)=-0.217$) than that for (VI)



(VI)

($q(N^1)=-0.204$) and accordingly (II) is more reactive than (VI), $\delta\Delta H^*=\Delta H^*(VI)-\Delta H^*(II)=1.5$ kcal/mol and $\delta\Delta G^*=\Delta G^*(VI)-\Delta G^*(II)=1.5$ kcal/mol (Table 1). This apparent inconsistency can be resolved by considering the resonance electron withdrawing effects of N^1 and N^2 as shown in Scheme 2. The delocalization of the p-π oxygen lone pair electrons will be more efficient in (II) since the three resonance structures, (A), (B) and (C), are possible for (II) compared to only two for (VI), (A) and (B). As a result, the two nitrogen atoms become more negative and the oxygen atom becomes more positive (or less negative) in (II) compared to those corresponding atoms in (VI) (Table 2). Thus



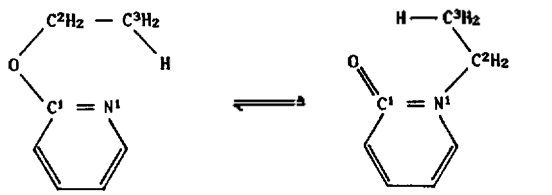
Scheme 2

the nucleophilicity of N^1 becomes greater and the C^2-O bond breaks more readily in (II) than in (VI), as evidenced by the gas-phase experimental rate constants for the two compounds, $k(II)=0.262\times10^{-3}$ sec^{-1} and $k(VI)=0.255\times10^{-3}$ sec^{-1}.[12]

2-Alkoxypyrazines, (III). In this compound, unlike in (II), the substituent nitrogen atom (N^2) is located at meta to the alkoxy group so that the p-π conjugation between O and N^2 is impossible. This means that the inductive electron withdrawing effect alone is operative in (III) and hence the electron density on N^1 will be less in (III) ($q(N^1)=-0.175$) than in (VI) ($q(N^1)=-0.204$) and accordingly the reactivity of (III) is lower than that of (VI), $\delta\Delta H^*=\Delta H^*(III)-\Delta H^*(VI)=0.8$ kacl/mol and $\delta\Delta G^*=\Delta G^*(III)-\Delta G^*(VI)=0.7$ kcal/mol. The gas-phase experimental rate constants are also in agreement with the lower reactivity expected, $k(III)=0.139\times10^{-3}$ sec^{-1} and $k(VI)=0.7$ kcal/mol. The gas-phase experimental rate constants are also in agreement with the lower reactivity expected, $k(III)=0.139\times10^{-3}$ sec^{-1} and $k(VI)=0.255\times10^{-3}$ sec^{-1}.[12]

4-Ethoxypyrimidine, (IV). In this compound, the substituent nitrogen, N^2, is at para position relative to the ethoxy group so that both the inductive and resonance effects are expected to be similar to those in the compound (II). Thus compared to (IV), this compound has a greater charge density on N^1 ($q(N^1)=-0.236$ for (IV) and $q(N^1)=-0.204$ for (VI)) and a lesser charge density on O ($q(O)=-0.202$ for (IV) and $q(O)=-0.210$ for (VI)) as a result of a greater p-π conjugation. Accordingly this compound is more reactive than (VI), $\delta\Delta H^*=\Delta H^*(VI)-\Delta H^*(IV)=0.5$ kcal/mol and $\delta\Delta G^*=\Delta G^*(VI)-\Delta G^*(IV)=2.2$ kcal/mol, which is consistent with the experimental rate constants of $k(IV)=0.285\times10^{-3}$ sec^{-1} and $k(VI)=0.255\times10^{-3}$ sec^{-1}.[15]

3-Ethoxypyridazine, (V). In this compound the substituent nitrogen, N^2, is at meta-position relative to the ethoxy group, so that the effect of N^2 can be expected to be approximately the same as that in (III) above. However, since N^2 is located at the neighboring, ortho-position to the N^1 atom, the charge density on N^1 is less negative due to a stronger inductive electron withdrawing effect than that for (VI) as well as for (III) ($q(N^1)=-0.110$ for (V) compared with $q(N^1)=-0.204$ for (VI) and $q(N^1)=-0.175$ for (III) in Table 2). We therefore predict based on these charge densities that the reactivity will be the lowest among the compound studied, i.e., (II)-(V), including (VI). However this prediction turns out to be quite wrong, since the gas-phase experimental results of Al-Awadi *et al.*[15] have shown that the compound (V) has *abnormally* high reactivity and is actually the most reactive one, $k(V)=2.56\times10^{-3}$ sec^{-1} which is *ca.* 10-times of the rate for (VI), $k(VI)=0.255\times10^{-3}$ sec^{-1}. They attributed this anomaly to the exceptionally high C^1-N^1 bond order (short C^1-N^1 bond length) in pyridazine. They estimated bond lengths for pyridine and the diazines and shown that the bond lenght of C^1-N^1 is the shortedst in pyridazine; the higher bond order therefore is expected to lead to the stronger nucleophilicity of the C^1-N^1 π-bond giving a faster reaction. In contrast, however, according to our all optimized AM1 geometries in Table 3, the bond length of C^1-N^1 is actually the longest for (V), which is quite opposite to what they claimed. It is thus natural that the longest bond length (the smallest bond order) of C^1-N^1 for (V) leads to the least reactivity as our calculations have predicted. As A-Awadi *et al.* has pointed out in their experimental work,[15] the high reactivity of (V) is an anomaly, but their rationalization by the high bond order of $C^1=N^1$ is clearly untenable. Perhaps the cause for this disagreement between experiment and theory can be clarified through careful further experiment and/or by a higher level *ab initio* calculations. We can rule out the possibility of decomposition through N-alkylated tautomer. For the pyridine analogue, (VI), the activation barrier to the ethyl migration process, Eq. (2), was $\Delta H^{\neq}=72.3$ kcal/mol, which is higher than the barrier to the decomposition process.[16] By similar reasoning the decomposition mechanism through N-alkylated tautomer for species (V) can also be



(VI) (2)

excluded as untenable. Thus the results of our calculation, i.e., the lowest reactivity predicted, is in direct contradiction to the abnormally high reactivity of (V) found experimentally by Al-Awadi *et al.*[15]

Albeit it is well known that the thermal decomposition processes proceed by a concerted process with the six membered cyclic TS (Eq. (1)), it does not necessarily mean that the two bond cleavage processes of the C^2-O and C^3-H bonds are synchronous. In the present work, if they were synchronous the magnitudes of Δd (or Δq) for the C^2-O and C^3-H bond cleavage processes should be proportional. Refernece to Table 3 reveals that the magnitude of Δd for C^2-O bond cleavage decreases in the order $(R^1=R^2=Me)>(R^1=H,\ R^2=Me)>(R^1=R^2=H)$ whereas that for C^3-H bond cleavage is in the reverse order. Thus the two bond cleavage processes may be concerted, but are certainly not synchronous and occur in successive stages. This is consistent with the results of experimental as well as theoretical studies on esters,[2,3] imines and amides.[4,5] There still remains however, a controversial problem as to which stage is rate limiting. According to the arguments presented by Al-Awadi *et al.*, C^2-O bond cleavage is the rate determining step.[2a-c] On the contrary, we propose that C^3-H bond cleavage is rate limiting on the following ground.[3,4] The greater the magnitude of Δd (or Δq), the greater should be the deformation energy required and hence the higher will be the activation enthalpy, ΔH^{*}. Examination of Table 1-3 indicates that the activation enthalpy is in the reverse order to that required by Δd (or Δq) for C^2-O bond cleavage but is consistent with that required by Δd (or Δq) for C^3-H bond cleavage. This strongly suggests that bond cleavage of the C^3-H bond is rate limiting,[17] as we have already concluded in our previous theoretical studies on the thermal decomposition mechanisms of esters and their nitrogen analogues.[3,4]

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