

AM1 Studies on the Gas-Phase Pyrolysis of Iminoethers, 2-Alkoxyridines, 2-N-Alkylated Pyridones and N-Alkylated Acetamides¹

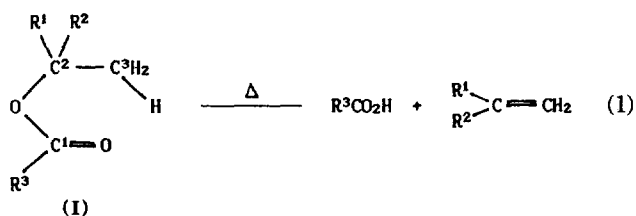
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The gas-phase pyrolysis reactions of iminoethers (II), 2-alkoxyridines (III), 2-N-alkylated pyridones (IV) and N-alkylated acetamides (V) have been studied MO theoretically with the AM1 method. The decomposition of these compounds proceeds by a concerted retro-ene process through a six-membered cyclic transition state. The reactivity decreases in the order (II)>(III)>(IV)>(V), with a greater reactivity for the imine series, (II) and (III), compared to the amide series, (IV) and (V), and a difference in basicity between the N and O atoms. Within a given series, however, the reactivity is dictated mainly by the aromaticity in the transition state. The reactivity order with respect to side alkyl chain of a species was found to increase as the steric crowding effect increases. The AM1 reactivity in this work agree well with the experimental results.

Introduction

Gas-phase thermal decomposition of esters (I), Eq. (1), has been widely studied both experimentally² and theoretically,³ and the reaction is known to proceed by a concerted process through a six-membered cyclic transition state (TS). However, relatively few works have, as yet, been reported on the thermal decomposition reactions of imines and amides, which are the nitrogen analogues of esters.



In this work, we carried out theoretical investigations of reactivities of such compounds, (II)-(V), using the AM1 MO method.⁴ The reactivities of these compounds have various interesting aspects. We can look at the effects of replacing a carbonyl or alkoxy oxygen in esters, (I), by a nitrogen on the reactivity of thermal decomposition. It is also interesting to compare the reactivities between (II) and (V), and between (III) and (IV), in which the heteroatoms N and O are exchanged; in (II) and (III) a C-O bond is cleaved and an N-H bond is formed whereas in (IV) and (V) a C-N bond is broken and a O-H bond is formed in the reaction.

On the other hand, the decomposition of (III) proceeds similarly with (II), while the reaction of (IV) is similar to that of (V). In the TS, aromaticity of pyridine ring in (III) is being removed whereas that of the ring in (IV) is being

introduced, and no such change in the aromaticity of a ring is involved in the TS with (II) and (V). The reactivity of thermal decomposition has been shown to increase experimentally⁵ and theoretically⁶ for these compounds when side alkyl chains are introduced by substituting methyl group, *i.e.*, $R^1=R^2=CH_3$. This rate enhancement is generally ascribed to (i) stabilization of C²-carbonium ion by electron donating effect of the methyl group and (ii) steric acceleration of rate by the methyl group in the TS. We have considered all these aspects MO theoretically in this work.

Calculations

The AM1 procedure⁷ 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 coordinated method,⁹ refined by the gradient norm minimization method,¹⁰ and characterized by confirming only one negative eigenvalue in the Hessian matrix.⁸ The activation entropy, ΔS^\ddagger , was obtained by subtracting the calculated entropy of the ground state from that of the TS at 600 K, using a program incorporated with in the AMPAC.

Results and Discussion

The activation parameters, ΔH^\ddagger , ΔS^\ddagger and ΔG^\ddagger , and heats of reaction (ΔH_R) for the thermal decomposition processes of (II)-(V) are summarized in Table 1. Examination of this Table reveals that for all cases, (II)-(V), the reactivity increases with methyl substitution, ($R^1=R^2=H$) < ($R^1=H$, $R^2=Me$) < ($R^1=R^2=Me$). This reactivity order is consistent with the gas-phase results of Taylor *et al.* for (III).¹¹ Although direct comparisons with experimental results are not possible for other compounds due to lack of the experimental data, the results for esters and other related reactions suggest that the methyl substitution at the C²-position enhances the reactivity as our AM1 results indicated.⁶ We note in Tables 2 and 3 that this enhancement of reactivity due to the methyl substitution, *i.e.*, R^1 and/or R^2 are CH_3 , is not originated from

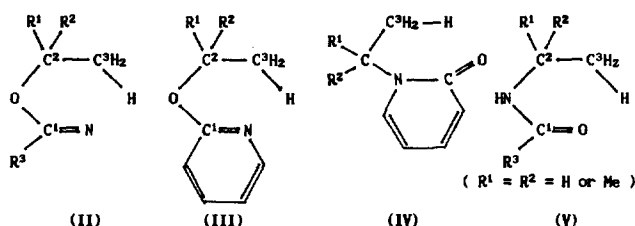
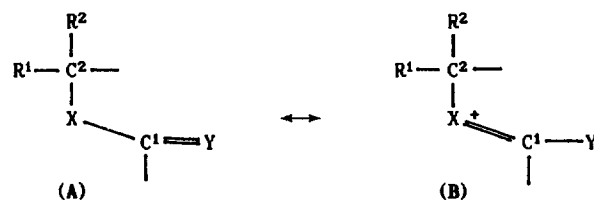


Table 1. The AM1 Activation Parameters for The Thermal Decomposition Processes of The Compounds II-V

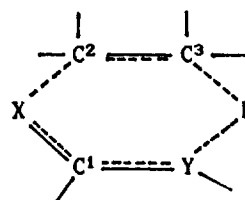
Compound	Substituents	Activation parameters ^a			ΔH_R^a
		ΔH^{*b}	ΔS^{*c}	ΔG^{*d}	
II	R ¹ =R ² =H	48.3	-4.2	50.8	2.5
	R ¹ =H, R ² =Me	46.2	-2.2	47.5	-5.3
	R ¹ =R ² =Me	45.1	-4.0	47.5	-11.1
III	R ¹ =R ² =H	56.5	-2.9	58.2	16.1
	R ¹ =H, R ² =Me	53.7	-2.2	55.0	9.3
	R ¹ =R ² =Me	50.6	+1.4	49.8	1.5
IV	R ¹ =R ² =H	58.9	-3.5	61.0	15.4
	R ¹ =H, R ² =Me	57.5	-2.0	58.7	7.9
	R ¹ =R ² =Me	56.4	-0.2	56.5	-0.2
V	R ¹ =R ² =H	67.5	-1.0	68.1	31.7
	R ¹ =H, R ² =Me	65.3	-1.2	66.0	24.2
	R ¹ =R ² =Me	65.6	+1.0	65.0	18.7

^a $\Delta H_R = \Delta H_f$ (Product complex) - ΔH_f (Reactant) in kcal/mol. ^b $\Delta H^* = \Delta H_f$ (TS) - ΔH_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.

stabilization of the positive charge developed at C²-position in the TS by electron donating ability of the Me-group, but is possibly originated from steric effect. In the ground state (GS) the successive substitution methyl group at C² leads to an increase in steric congestion since C² forms an sp³ center. In the TS, however, the C²-atom will have an intermediate hybrid character between that of sp³ and sp² so that the steric congestion becomes partially released and results in the increased reactivity. This steric release in the TS with the methyl substitution except for V is reflected in a greater degree of bond breaking of the C²-X (X=O or N) bond with the successive methyl substitution as can be seen in



Scheme 1.



Scheme 2.

Tables 4 and 5. Moreover, the heats of reaction in Table 1 indicate that the product, olefin, becomes more stable with the methyl substitution at C² rendering a greater exothermicity (or a lesser endothermicity) which should be in favor of a greater reactivity thermodynamically. However, in the case of V, the steric release in the TS with the methyl substitution is not significant, because the high endothermicity for the elimination reaction of V, due to the unstability of one of the product, imino alcohol, makes the TS later one comparing with IV. ($\Delta d = 0.135 \text{ \AA}$ for IV, R¹=R²=H, and $\Delta d = 0.229 \text{ \AA}$ for R¹=R²=H).

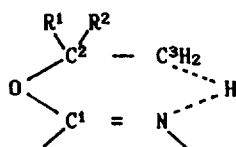
Reference to Table 1 indicates that for the case of Y=N the species (II) is more reactive than (III). The following reasons can be given for this reactivity difference: (i) The basicity of the N-atom and hence the nucleophilicity of N toward the hydrogen atom on C³ for (III) is less than that for (II) as the lower negative charge of N in the GS for (III) implies (Table 2). (ii) Electron deficiency at atom X due to *p*- π conjugation¹² (Scheme 1) weakens the σ -bond of

Table 2. Charges (q) on the heavy atoms and H(C³-H) for the compounds I and II at GS and TS in electronic charge unit

Compound	Substituents		N	C ¹	O	C ²	C ³	H
II	R ¹ =R ² =H	GS	-0.328	+0.117	-0.233	-0.009	-0.243	+0.097
		TS	-0.333	+0.231	-0.305	+0.089	-0.643	+0.317
		Δq	-0.005	+0.114	-0.072	+0.098	-0.400	+0.220
	R ¹ =H, R ² =Me	GS	-0.328	+0.122	-0.236	+0.050	-0.239	+0.098
		TS	-0.341	+0.232	-0.319	+0.144	-0.625	+0.320
		Δq	-0.013	+0.110	-0.083	+0.064	-0.386	+0.222
	R ¹ =R ² =Me	GS	-0.330	+0.125	-0.236	+0.099	-0.233	+0.103
		TS	-0.360	+0.235	-0.336	+0.208	-0.609	+0.325
		Δq	-0.030	+0.110	-0.110	+0.109	-0.376	+0.222
III	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
	R ¹ =H, R ² =Me	GS	-0.204	+0.136	-0.213	+0.050	-0.238	+0.101
		TS	-0.260	+0.261	-0.383	+0.185	-0.592	+0.346
		Δq	-0.056	+0.125	-0.170	+0.135	-0.354	+0.245
	R ¹ =R ² =Me	GS	-0.206	+0.142	-0.216	+0.100	-0.234	+0.101
		TS	-0.310	+0.259	-0.444	+0.274	-0.514	+0.345
		Δq	-0.104	+0.117	-0.218	+0.174	-0.280	+0.244

Table 3. Charges (q) on The Heavy Atoms and H(C³-H) for The Compounds III and IV of GS and TS in Electronic Charge Unit

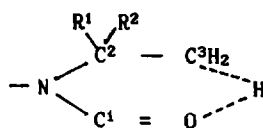
Compound	Substituents		O	C ¹	N	C ²	C ³	H
IV	R ¹ =R ² =H	GS	-0.370	+0.323	-0.236	-0.044	-0.232	+0.093
		TS	-0.289	+0.247	-0.156	+0.085	-0.708	+0.332
		Δq	+0.081	-0.076	+0.080	+0.129	-0.476	+0.239
	R ¹ =H, R ² =Me	GS	-0.373	+0.326	-0.234	+0.034	-0.232	+0.116
		TS	-0.300	+0.252	-0.159	+0.139	-0.707	+0.334
		Δq	+0.073	-0.074	+0.075	+0.105	-0.475	+0.218
	R ¹ =R ² =Me	GS	-0.376	+0.325	-0.226	+0.081	-0.228	+0.119
		TS	-0.302	+0.258	-0.165	+0.195	-0.703	+0.337
		Δq	+0.074	-0.067	+0.061	+0.114	-0.475	+0.218
V	R ¹ =R ² =H	GS	-0.369	+0.297	-0.381	-0.033	-0.239	+0.084
		TS	-0.269	+0.202	-0.285	+0.175	-0.638	+0.297
		Δq	+0.100	-0.095	+0.096	+0.208	-0.399	+0.213
	R ¹ =H, R ² =Me	GS	-0.372	+0.303	-0.389	+0.045	-0.235	+0.107
		TS	-0.276	+0.221	-0.286	+0.135	-0.674	+0.309
		Δq	+0.096	-0.082	+0.103	+0.090	-0.439	+0.202
	R ¹ =R ² =Me	GS	-0.376	+0.306	-0.386	+0.090	-0.228	+0.107
		TS	-0.284	+0.234	-0.290	+0.192	-0.690	+0.318
		Δq	+0.092	-0.072	+0.096	+0.102	-0.462	+0.211

Table 4. Bond Lengths for The Compounds I and II of GS and TS in Å

Compound	Substituents		N-C ¹	C ¹ -O	O-C ²	C ² -C ³	C ³ -H	N-H
II	R ¹ =R ² =H	GS	1.289	1.385	1.431	1.509	1.116	2.736
		TS	1.338	1.317	1.602	1.416	1.618	1.107
		Δd	+0.049	-0.068	+0.171	-0.093	+0.502	-1.629
	R ¹ =H, R ² =Me	GS	1.289	1.381	1.435	1.514	1.115	2.740
		TS	1.336	1.317	1.642	1.423	1.571	1.129
		Δd	+0.047	-0.064	+0.207	-0.091	+0.456	-1.611
	R ¹ =R ² =Me	GS	1.289	1.380	1.447	1.520	1.115	2.590
		TS	1.333	1.315	1.693	1.430	1.517	1.157
		Δd	+0.044	-0.065	+0.246	-0.090	+0.402	-1.433
III	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
	R ¹ =H, R ² =Me	GS	1.357	1.377	1.438	1.514	1.116	2.650
		TS	1.380	1.305	1.790	1.413	1.490	1.183
		Δd	+0.023	-0.072	+0.352	-0.101	+0.374	-1.467
	R ¹ =R ² =Me	GS	1.357	1.374	1.449	1.520	1.114	2.599
		TS	1.380	1.299	1.962	1.422	1.358	1.314
		Δd	+0.023	-0.075	+0.513	-0.098	+0.244	-1.285

the C²-X bond, which is cleaved in the TS, and as a result the greater the contribution of (B), the easier is the breaking of the C²-X bond and hence the greater will be the reactivity. Contribution of resonance structure (B) in Scheme 1 will be less in the GS of (III) compared to that of (II) since this structure will cause a loss of aromaticity of the pyridine

ring, which should result in a lesser reactivity. (iii) The six-membered cyclis TS (Scheme 2) for these reactions requires a greater destabilization due to partial loss of aromaticity of the pyridine ring for (III), in contrast to no such change in the aromaticity for (II), leading to a lesser reactivity for (III).

Table 5. Bond Lengths(d) for The Compounds I and II of GS and TS in Å

Compound	Substituents		O-C ¹	C ¹ -N	N-C ²	C ² -C ³	C ³ -H	O-H
IV	R ¹ =R ² =H	GS	1.248	1.418	1.451	1.520	1.116	3.608
		TS	1.345	1.374	1.586	1.406	1.719	1.030
		Δd	+0.097	-0.044	+0.135	-0.114	+0.603	-2.505
	R ¹ =H, R ² =Me	GS	1.248	1.419	1.466	1.529	1.118	2.369
		TS	1.343	1.374	1.614	1.415	1.688	1.037
		Δd	+0.095	-0.045	+0.148	-0.114	+0.570	-1.332
	R ¹ =R ² =Me	GS	1.249	1.422	1.481	1.539	1.117	2.257
		TS	1.340	1.375	1.654	1.422	1.646	1.047
		Δd	+0.091	-0.047	+0.173	-0.117	+0.529	-1.210
V	R ¹ =R ² =H	GS	1.247	1.384	1.437	1.522	1.116	3.671
		TS	1.359	1.311	1.666	1.380	1.994	0.989
		Δd	+0.112	-0.073	+0.229	-0.142	+0.878	-2.682
	R ¹ =H, R ² =Me	GS	1.248	1.381	1.448	1.531	1.118	2.508
		TS	1.355	1.312	1.657	1.394	1.901	0.999
		Δd	+0.107	-0.069	+0.209	-0.137	+0.783	-1.509
	R ¹ =R ² =Me	GS	1.248	1.379	1.460	1.539	1.117	2.449
		TS	1.351	1.313	1.675	1.405	1.825	1.009
		Δd	+0.215	-0.134	+0.708	-1.440		

Table 6. Ground State HOMO-LUMO Energy Levels for The Compounds I-IV in eV

Compound	Substituents	$\epsilon_{\text{HOMO}(1)}^a$	$\epsilon_{\text{HOMO}(2)}^b$	ϵ_{LUMO}^c	$\Delta\epsilon_{\text{FMO}(1)}^d$	$\Delta\epsilon_{\text{FMO}(2)}^d$
II	R ¹ =R ² =H	-10.41	-10.76	5.21	15.62	15.97
	R ¹ =H, R ² =Me	-10.32	-10.56	5.23	15.55	15.79
	R ¹ =R ² =Me	-10.29	-10.56	5.33	15.62	15.89
III	R ¹ =R ² =H	-9.25	-10.70	5.11	14.36	15.81
	R ¹ =H, R ² =Me	-9.19	-10.58	5.18	14.37	15.76
	R ¹ =R ² =Me	-9.15	-10.56	5.23	14.38	15.79
IV	R ¹ =R ² =H	-12.52	-10.73	4.73	17.25	15.46
	R ¹ =H, R ² =Me	-12.52	-10.52	5.06	17.58	15.58
	R ¹ =R ² =Me	-12.80	-10.47	5.11	17.90	15.58
V	R ¹ =R ² =H	-15.92	-10.78	4.91	20.83	15.69
	R ¹ =H, R ² =Me	-15.75	-10.47	5.20	20.95	15.67
	R ¹ =R ² =Me	-15.79	-10.48	5.24	21.03	15.72

^aHOMO(1) is a π -bonding orbital of C¹=Y bond. ^bHOMO(2) is a σ -lone pair orbital of Y-atom. ^cLUMO is a σ^* -antibonding orbital of C³-H bond. ^d $\Delta\epsilon_{\text{FMO}}(i) = \epsilon_{\text{LUMO}} - \epsilon_{\text{HOMO}}(i)$.

On the other hand for the case of Y=O, reference to Table 1 reveals that compound (IV) is more reactive than (V). The reasons for this reactivity difference should be similar to those between (II) and (III) discussed above: (i) The nucleophilicity of O-atom toward the hydrogen of C³-H will be greater for (IV) than for (V) since the O-atom is more basic due to a greater negative charge. (ii) The contribution of the resonance structure (B) in Scheme 2 will be greater for (IV), since aromaticity of the pyridone ring is easily introduced in the TS as a result of p - π conjugation in the GS. A greater contribution of structure (B) will induce electron deficiency on the X-center and weakens the C²-X σ -bond le-

ading to a greater reactivity. (iii) Aromaticity introduced in the pyridone ring as the reaction progresses, (III) \rightarrow TS \rightarrow Products, stabilizes (IV) compared to (V) for which no such stabilizing effect is possible. This is in contrast to the reactivity difference incurred by a loss of aromaticity in (III) relative to (II), which does not involve such aromaticity change.

Comparison of reactivity in Table 1 between (II) and (V), and between (III) and (IV), for which the two heteroatoms X and Y are interchanged, indicates that the imine system, (II) and (III), are more reactive than the amide system (IV) and (V). This is consistent with the general trend that amides are relatively unreactive with respect to the elimination

reaction.¹³ The lower reactivity of amides than imine can be readily rationalized. It has been shown MO theoretically by Lee *et al.*¹⁴ that in the 1,*n*-sigmatropic rearrangements the nucleophilicity of Y=N (imines) is greater than Y=O (amides). Furthermore the frontier MOs (FMOs) of the GS, *i.e.*, the HOMOs, the σ -lone pair orbital of Y-atom and the π -HOMO of C¹=Y, and σ^* -LUMOs of C³-H, in Table 6 show that the HOMO levels of the imine system (C=N π -bond) are higher than those for the amide system (the lone pair orbitals of O-atom). According to the perturbation MO (PMO) theory¹⁵ the FMO energy gap is narrower for the imines leading to a greater charge transfer (ϵ_{ct}) stabilization¹⁶ in the TS. Examination of atomic charges in Tables 2 and 3 reveal that the HOMO for (II) and (III) is the π -orbital of C=Y, while that for (IV) and (V) is the lone pair orbital of O so that in the activation process for (II) and (III), the C¹-atom becomes more positive whereas for (IV) and (V) the Y(=O) atom becomes more positive as a result of charge transfer to the LUMO of the C³-H bond. On the other hand negative charge develops on the C³-atom whereas positive charge develops on the H-atom in the TS, indicating that the C³-H bond is being heterolyzed *i.e.*, the proton is being transferred, by accepting electrons into the σ^* -antibonding LUMO. These FMO and charge density analysis show that the nucleophilicity (or basicity) of the Y-atom is the major factor determining the reactivity.

In general, entropy factor is small in the thermal decomposition of the compounds studied, but methyl substitution seems to result in favorable ΔS^* term due mainly to a greater degree of bond cleavage in the TS for the methyl substituted compounds. This is another manifestation of steric releasing effect of the sterically congested compounds in the GS.

Finally, the thermal decomposition process discussed above may not be a synchronous one albeit it can proceed concertedly through a six-membered cyclic TS. The changes in formal charges of heavy atoms and bond lengths in Tables 2 and 3 do not support proportional changes in bond polarization (Δq) and bond length (Δd) for the two cleaving bonds of C²-X and C³-H. For example, Δd decreases in the order (R¹=R²=Me) > (R¹=H, R²=Me) > (R¹=R²=H) for the C²-X bond breaking process, but it is in the order, (R¹=R²=H) > (R¹=H, R²=Me) > (R¹=R²=Me) for the C³-H bond cleavage. The two bond breaking processes may be concerted but are not certainly synchronized, in agreement with the experimental results of Taylor *et al.*^{2(a)-(d),5,11} and with the theoretical predictions of Lee *et al.*^{3,6}

In these successive two-step mechanism, there is still a problem of deciding which step is the rate determining one. Some investigators argued in favor of the C³-X bond cleavage,^{2(a)-(c)} while others favor the C³-H bond cleavage as the rate limiting step.^{13,17} However in the present systems, the latter proposal is supported: the greater the values of Δq and Δd are, the greater will be the required deformation energy in the activation process, *i.e.*, higher ΔH^* values. Close examination of Tables 2-5 reveals that the variations of Δq and Δd are in reverse order in the C²-X bond cleavage process whereas they show parallel trend for the C³-H bond cleavage. Thus the C³-H bond breaking step should be rate limiting, which is again in agreement with the results of

our previous works on the thermal decomposition of esters and also with the substantial kinetic isotope effect for the C³-H(D) bond cleavage ($k_H/k_D=2.1$) observed experimentally.^{13,17}

Acknowledgement. We thank the Ministry of Education and the Research Center for Theoretical Physics and Chemistry for support of this work.

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