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THEORETICAL STUDIES ON THE ACYLATION REACTIONS OF AMMONIA BY KETENES: DETERMINATION OF REACTIVITY BY MOLECULAR ORBITAL THEORY (PART 54)

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ABSTRACT

Theoretical studies on the reactions of ammonia with ketene and dimethylketene using the MNDO method are reported. The single step addition of ammonia to the olefinic bond of ketenes was found to provide a lower energy-barrier path than the two step carbonyl addition mechanism. The barrier height was lower in the reaction of keten compared with that of dimethylketene in support of the faster rate of solution phase reactions of aniline and ketenes. The deformation energies of reactants had an overwhelming influence in determining the activation barriers in all the reactions investigated.

INTRODUCTION

Acylation reactions of carboxylic acids, alcohols, and amines by ketenes have been widely studied owing to their industrial importance.[1] Blake and Davies[2] reported the gas phase kinetic studies on the addition of ketene to acetic acid to give acetic anhydride and proposed a six-center cyclic transition state (TS) formed by attachment of the carbonyl oxygen of the acid to the carbonyl carbon of ketene. On the other hand, Lillford and Satchell[3] found for the reaction in ether of *m*-chloroaniline with ketene that the rate equation has the form given by equation (1).

$$\text{rate} = (k_1[\text{ArNH}_2] + k_2[\text{ArNH}_2]^2)\,[\text{ketene}] \qquad (1)$$

This indicates the involvement of a path with one aniline molecule in the TS in addition to the dimer participation.[4] They concluded that the reaction proceeds via a straightforward single step addition to the olefinic bond with the TS of structure (**1**).

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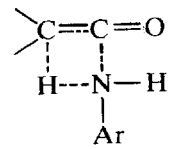
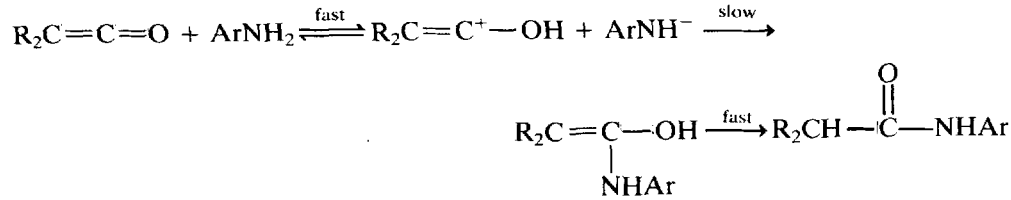


(1)

In order to account for the low reactivity of dimethylketene relative to ketene, however, they considered the possibility of a carbonyl addition mechanism in which an ion-pair intermediate is formed prior to the rate determining attack on the α-carbon, as shown in Scheme 1.[3]



Scheme 1

Their HMO calculations on the atomic charge distributions indicated that the negative charge on the carbonyl oxygen of ketene is greater than that of dimethylketene, and the carbonyl oxygen has a greater negative charge than the β-carbon atom in both compounds (Table 1).

Table 1. Comparison of geometrical parameters and atomic charge distributions of ketene and dimethylketene[a] ($R_1R_1C_2{=}C_3{=}O_4$)

	Method	Geometrical Parameters				Atomic Charges				Reference
		d_{12}	d_{23}	d_{34}	$L123$	1	2	3	4	
Ketene	MNDO	1.085	1.319	1.184	121.78	+0·09	−·28	+0·26	−0·17	This work
	ab initio					+0·22	−0·53	+0·24	−0·14	10
	HMO						−0·22	+0·49	−0·41	3
	Experim.	1·071	1.314	1.161	119·00					11
Dimethyl-	MNDO	1–503	1.330	1.181	120·56	+0·09	−0·35	+0·31	−0·16	This work
Ketene	HMO						−0·09	+0·47	−0·39	3

[a]d in Å, angle in degree and charge in a.u.

In this work, in order to examine the mechanism of acylation reactions of amines by ketene, we have carried out the MNDO computations[5a] on the reactions of ketene and dimethylketene with ammonia.

CALCULATIONS

The calculations were carried out using the standard MNDO procedure. Geometries of all species at stationary points on the potential energy surface were fully optimized using the

Davidon–Fletcher–Powell method.[5b,c] Transition states were located by the reaction coordinate method,[6] refined by the gradient norm minimization[7] and characterized by confirming only one negative eigenvalue in the Hessian matrix.[8] The TSs were also confirmed by the downhill energy optimization in both directions along the reaction coordinate to find the appropriate reactants, intermediates, and products.

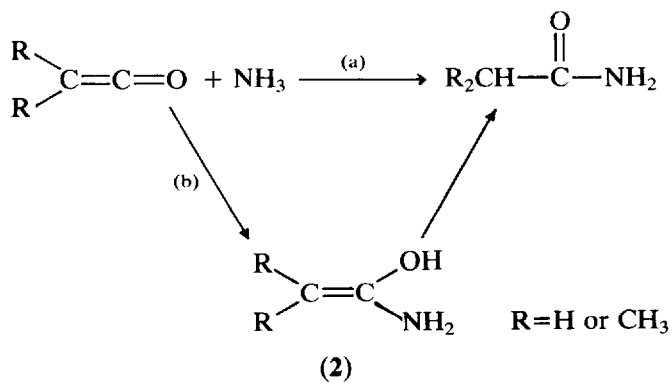
Zero-point energies, entropies, and enthalpy corrections for temperature changes were calculated using the procedures implemented in the AMPAC programs.[9]

RESULTS AND DISCUSSION

The optimized geometries and atomic charges of ketene and dimethylketene are compared with experimental and other MO results in Table 1. The MNDO geometries are seen to agree satisfactorily with those of the experimental values. Moreover our MNDO atomic charge distributions exhibit similar trends to those of the *ab initio* calculations. In contrast, the HMO atomic charges show a notable discrepancy as to the relative magnitude of negative charges on the carbonyl oxygen and the β-carbon atom. This is an important aspect with regard to the probable reaction path, since a greater negative charge on the carbonyl oxygen would favor the carbonyl addition mechanism in Scheme 1, whereas a greater negative charge on the β-carbon will favor the addition to the olefinic bond with the structure (**1**). In order to investigate the protonation behaviour of the ketenes, we have compared relative stabilities of the three protonated tautomers in Table 2. In excellent agreement with the *ab initio* values, our MNDO results predict the β-carbon protonation to be the most preferred form. It is therefore unlikely that an ion-pair is formed by protonating the carbonyl oxygen as in Scheme 1. In this work, we have disregarded the ion-pair intermediate and considered two paths : a single-step path, (a), and a two-step path, (b), which involves an intermediate (**2**) as shown in Scheme 2.

Table 2. Relative energies of protonated ketene tautomers (in kcal/mol)

	β-C—H$^+$	α-C—H$^+$	O—H$^+$
MNDO	0	56·2	26·7
ab inition[11]	0	58·2	29·2



(**2**)

Scheme 2

We will adopt abbreviations K-a, K-b and DK-a, DK-b for the reaction paths a and b of ketene (K) and dimethylketen (DK), respectively.

The potential energy profiles for K-a and K-b, and DK-a and DK-b are presented in Figures 1 and 2. In order to compare our results with the solution-phase data, we have calculated the Gibbs free energy of activation, $\Delta G^{\neq}$, by evaluating zero-point energies, Z_O, entropies, S, and enthalpy corrections for the temperature changes, ΔH_T, in addition to the heats of formation, ΔH_f. The results are summarized in Table 3. For the two-step path, (b), the $\Delta G^{\neq}$ values are evaluated only for the first step corresponding to TS1, although the barrier for TS1 is actually lower than that for the second step, TS2. Yet in both cases, i.e., for K-b and DK-b, the computed $\Delta G^{\neq}$ values indicate that the first step, TS1, in path (b) is unfavorable compared with that in path (a), i.e., K-a and DK-1. Thus the energetics favours the single step path, (a), over path (b), in agreement with the conclusion reached experimentally by Satchell *et al.* Moreover path (b) has an intermediate which is more stable than the reactants and hence the rate equation (1) does not apply.[12] This conclusion will be strengthened and become more obvious if we take into consideration the even higher second activation barrier, TS2, in path (b). The 1,3-hydrogen shifts involved in the second step of path (b) for both ketene and dimethylketene have activation barriers nearly equivalent to those of the similar processes obtained by the *ab initio* calculations,[13] indicating that the deficiency of the MNDO method in handling the hydrogen bond energies[14] does not seem to matter in these types of problems.

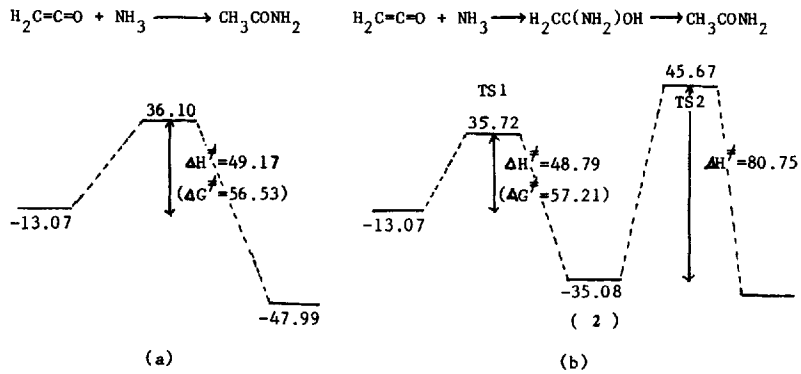


Figure 1. Energy profiles of (a) reaction K-a and (b) reaction K-b (in kcal/mol)

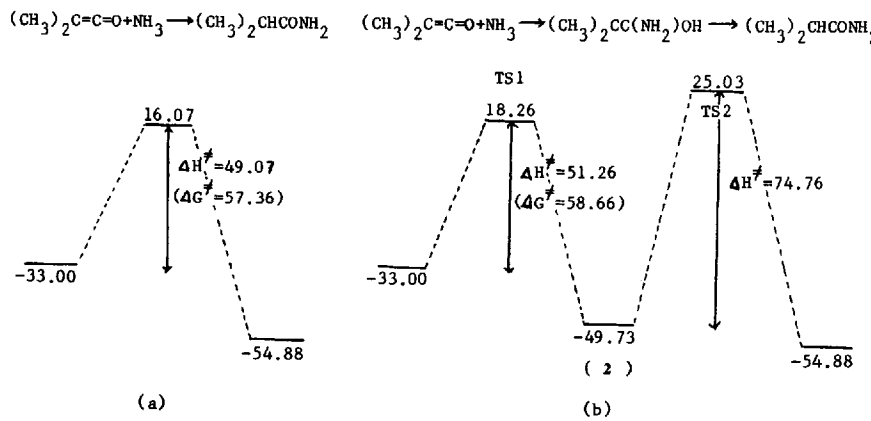


Figure 2. Energy profiles of (a) reaction DK-a and (b) reaction DK-b (in kcal/mol)

Table 3. Heats of formation (ΔH_f), zero-point energies (Z_0), enthalpy corrections for temperature changes (ΔH_T), entropies (S), and activation free energies ($\Delta G^{\neq}$)[a] for species on stationary points (kcal/mol) in the reactions of ketenes and ammonia

Reaction Path[b]	Reactant				TS1				Interm (2)	TS2	Prod.	$\delta G^{\neq}$
	ΔH_f^0	Z_0	ΔH_T	S^c	ΔH_f	Z_0	ΔH_T	S^c				
K-a	−13·07	44·41	4·95	102·51	36·10	43·03	3·45	68·10			−47·99	56·53
K-b	−13·07	44·41	4·95	102.51	35·72	43·63	3·11	65·42	−35·05	45·67	−47·99	57·21
DK-a	−33·00	81·92	6·36	118·90	16·07	80·67	5·10	82·67			−54·88	57·36
DK-b	−33·00	81·92	6·36	118·90	18·26	80·24	5·11	84·25	−49·73	25·03	−54·88	58·66

[a]At 298K; [b]For abbreviations, see text.; [c]In cal/mol·K

Reference to Figures 1 and 2 also reveals that in all cases irrespective of the reaction path, ketene has a lower activation barrier $\Delta G^{\neq}$ than dimethylketene; this is again in agreement with the greater rate of reaction between keten and *m*-chloroaniline found experimentally.[3] It is also to be noted that the rate retardation with dimethylketene will be enhance due to a greater steric repulsion, especially in the reactions with a bulky reactant, *m*-chloroaniline. This steric repulsion may also contribute to a facile olefinic addition, (**3**), compared with the sterically crowded carbonyl addition, (**4**).

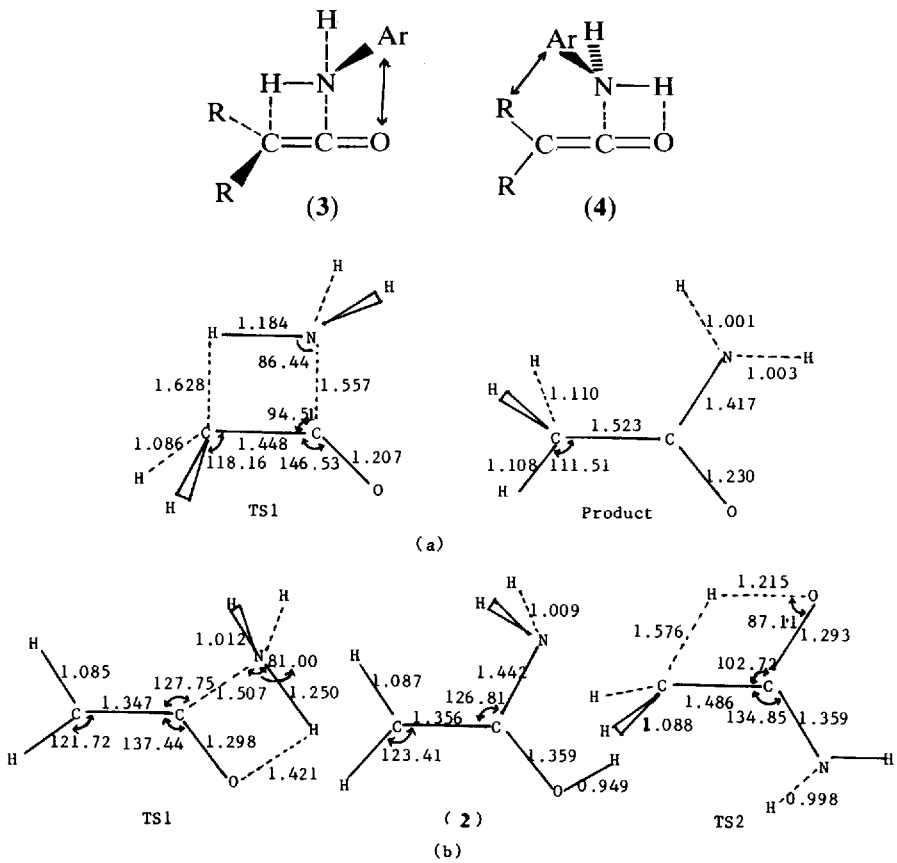


Figure 3. Stationary point structures of (a) reaction K-a and (b) reaction K-b (bond lengths in Å and angles in degree)

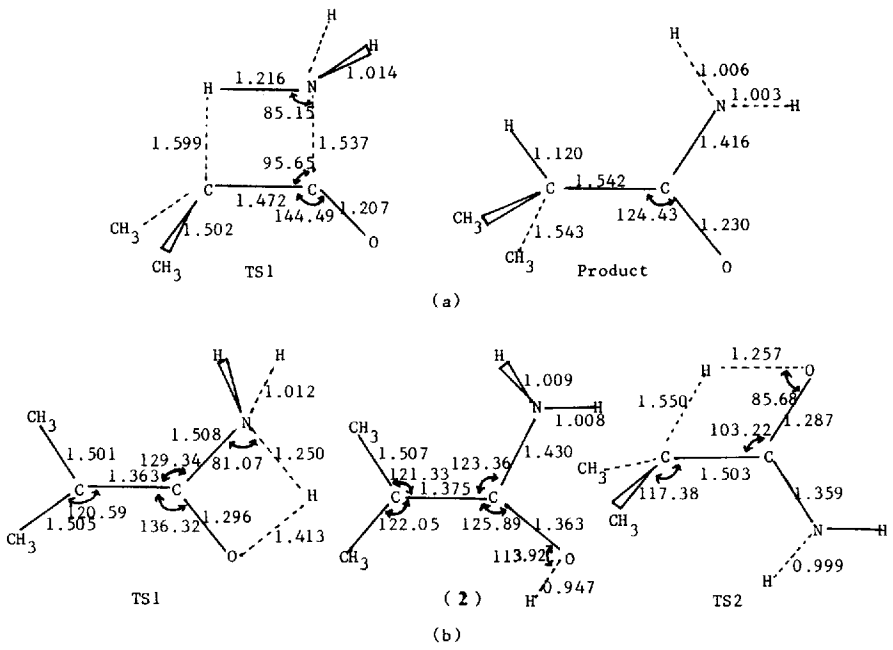
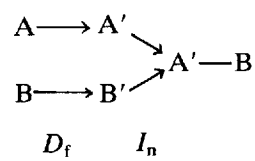


Figure 4. Stationary point structures of (a) reaction DK-a and (b) reaciton DK-b (bond lengths in Å and angles in degree)

Fully optimized stationary point geometries are presented in Figures 3 and 4 for ketene and dimethylketene reactions, respectively. Various other conformers are possible for products and intermediates, but the structures given in the Figures are those which are the most stable form. Inspection of the optimized structures in Figures 3 and 4 reveals : (i) the transition state of the first step (TS1) in all cases has a common four center cyclic structure. (ii) the structure of TS1 for the K-a process is more product-like than that for the DK-a process, demonstrating adherence to the Hammond postulate[15] in view of the greater exothermicity of K-a than DK-a (Figures 1a and 2a). (iii) Angular distortion of $\angle$CCO in the activation to TS1 is greater in path (b) than in path (a) due to the steric crowding in structure (**4**) above. (iv) the structure of the intermediates in path (b) are largely influenced by a dipole-dipole interaction between O—H and C—N bonds and the steric effect between CR_2 (R=H or CH_3) and NH_2 groups. (v) The structures of the products for the two reactions have a common feature that the nonbonding orbitals, n, on N interact effectively with the π^* orbital of the CO bond, (vi) the product in the dimethylketene reaction is formed so as to minimize the steric effect between the CH_3 group and the H of the amino group.

Useful mechanistic information can be obtained by the decomposition of activation energies into deformation, D_f, and interaction energies, I_n, as represented in Scheme 3.[16]



Scheme 3

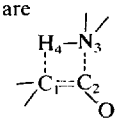
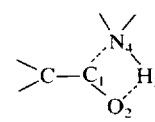
Table 4. Energy decomposition analysis for the reactions of ketenes and ammonia (kcal/mol)

Reaction Path[a]	D_f	I_n	$\Delta\Sigma 2\varepsilon_i$	$\Delta(V_{NN}-V_{ee})$
K-a	49.80	−0·62	−9·088	9·061
K-b	67·96	−19·16	−12·493	11·662
DK-a	58·34	−9·27	−5·289	4·887
DK-b	70·30	−19·04	−7·362	6·537

[a]For abbreviations, see text.

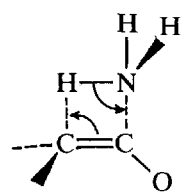
Table 5. Variation of atomic charges in the reactions of ketenes and ammonia[a] (a.u.)

Reaction Path[b]	Reactant				Deformed Fragment				TS1			
	1	2	3	4	1	2	3	4	1	2	3	4
K-a	−0·28	+0·26	−0·33	+0·08	−0·24	+0·24	−0·34	+0·14	−0·52	+0·41	−0·21	+0·24
K-b	+0·26	−0·17	+0·08	−0·23	+0·21	+0·20	−0·16	−0·38	+0·19	−0·44	+0·29	−0·18
DK-a	−0·35	+0·31	−0·23	+0·08	−0·32	+0·28	−0·36	+0·15	−0·56	+0·41	−0·22	+0·26
DK-b	+0·31	−0·61	+0·08	−0·23	+0·26	−0·19	+0·16	−0·38	+0·24	−0·43	+0·29	−0·19

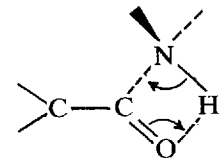
[a]Numbering schemes are  for K-a and DK-a and  for K-b and DK-b.; [b]For abbreviations, see text.

In this scheme A and B are the reactants, and A′ and B′ are the deformed fragments comprising the TS, A′—B′. The deformation and interaction energies are summarized in Table 4 for TS1 of the four reaction paths studied in this work. The interaction energies may be further subdivided into orbital energy changes, $\Delta\Sigma 2\varepsilon_i$, which reflect the effects of electron delocalization, non-bonded interactions etc.,[17] and repulsive energy changes, $\Delta(V_{NN} - V_{ee})$, which can be taken to account for the net steric repulsion effect in the activation.[18] The results in Table 4 clearly demonstrate the dominant influences, over 100%, of the deformation energy on the activation barrier, $\Delta H^{\neq}$; this is to be compared with ~70% contribution of D_f in the reaction of HCNO and H_2O[19] and ~20% in the reaction of $CH_2{=}C{=}NH$ with H_2O.[20]

Atomic charges are summarized in Table 5 for reactants, deformed fragments and TS1. Notable charge variations occuring in the formation of deformed fragments are the increases in negative charge on N and positive charge on the transferring H. This corresponds to an incipient electron shift involved in a partial scission of the N—H bond. On the other hand, the changes in atomic charges accompanied in the TS formation from the two fragments (i.e., the negative charge decrease on N, the positive charge increases on transferring H and α-carbon, and the negative charge increase on β-carbon) indicate that the lone pair on N is mobilized in the formation of a partial bond between N and α-carbon and the olefinic π bond begins to break transferring part of π electrons toward β-carbon (or carbonyl oxygen in path (b)). The electron shifts involved in the activation follow the exact patterns that are expected in the product formation as shown in **(5)** and **(6)**.



(5)



(6)

We conclude that the reactions of ammonia with ketenes take place through a single step addition to the olefinic bond, and the reactions are largely controlled by the deformation of reactants in the activation.

ACKNOWLEDGEMENTS

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