THEORETICAL STUDIES ON THE GAS-PHASE PYROLYSIS OF ACETIC ANHYDRIDE AND DIACETYL SULPHIDE*

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The gas-phase thermal decomposition of diacetyl compounds, $(CH_3CO)_2X$ with X = O and S, was investigated theoretically using the semiempirical MO methods MNDO and AM1. The initial decomposition of the diacetyl compounds proceeded through a six-membered ring transition state involving the keto form with a slightly lower activation enthalpy for diacetyl sulphide (X = S); the process via an enolic form of the transition state was kinetically unfavourable. In the initial decomposition of the diacetyl compounds and in the subsequent pyrolysis of acetic and thioacetic acid, ketene formation was found to be the most preferred path, where the ease of C_α—X bond cleavage is relatively more important than nucleophilic attack on the β-hydrogen in determining the overall reactivity. In the methane formation process, the reactivity was entirely dependent on the X—H bond strength in CH_3COXH where X = S, NH and O.

INTRODUCTION

Acetic anhydride (1, X = O) and diacetyl sulphide (1, X = S) are known to undergo thermal decomposition into ketene and acetic (or thioacetic) acid,[2] followed by further elimination into various products:[3]

$$O=C=CH_2 + CH_3COXH \quad \text{or}$$

$$CH_3CXOH \rightarrow \text{products} \quad (1)$$

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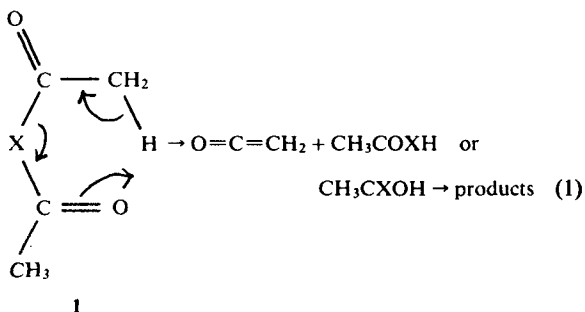
The initial gas-phase decomposition of diacetyl compounds, 1, into ketene and acetic (or thioacetic) acid has been experimentally investigated by Blake and Speis[4] and Taylor.[3] These two groups agreed that the transition state (TS) is a six-membered ring type for both compounds (X = O and S), but they differed in the relative order of the activation energy, which was in the

reverse order from 32·2 (X = O) and 31·3 kcal mol⁻¹ (X = S) in the former[4] to 34·8 (X = O) and 38·0 kcal mol⁻¹ (X = S) in the latter group.[3] This means that the rate of decomposition is faster with diacetyl sulphide than with acetic anhydride in the former, but is faster with acetic anhydride in the latter group, albeit the experimental temperature was higher in the latter work. Taylor[5] suggested that the faster rate of acetic anhydride decomposition, despite the greater bond strength of C_α—O bond than that of C_α—S, may be due to the involvement of an enolic TS, 2, and the enhanced nucleophilicity of the carbonyl group toward β-hydrogen by resonance with the ethereal oxygen, 3.

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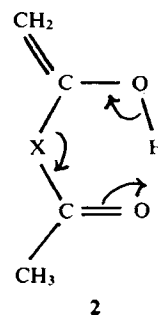
*Determination of Reactivity by MO Theory, Part 61. For Part 60, see Ref. 1.
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3   **4**   **5**
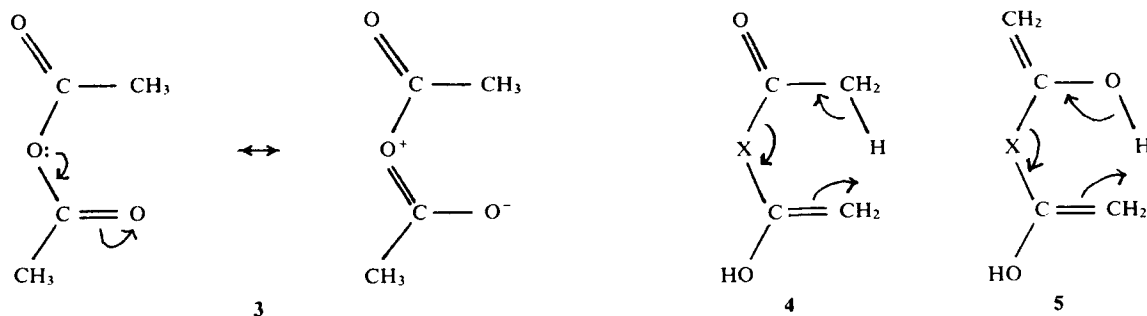
On the other hand, the products detected from the subsequent thermal decomposition of acetic[6] and thioacetic[3] acids were ketene, water, methane, carbon dioxide, and some of their thio analogues, e.g. H_2S and COS. In the thioacetic acid elimination, methanethiol was also found but no thioketene was detected.[3] Thioacetic acid had two forms, thiono- (CH_3CSOH) and thiolo- (CH_3COSH), and was much less stable than acetic acid.[7]

Recently, Dewar[8] introduced an effective semi-empirical MO procedure, AM1, which has a built-in allowance for electron correlation sufficient to deal with the changes that occur in most TS formation at far less cost than the comparable *ab initio* methods. The AM1 method is not as good as the 'state-of-the-art' *ab initio* method but it has the compensating advantage of being applicable to much larger molecules for which experimental data are available.

In this work, we investigated theoretically the gas-phase thermal pyrolysis mechanisms of acetic anhydride and diacetyl sulphide using the semiempirical MO methods AM1[9] and MNDO.[10]

CALCULATIONS

The computations were carried out using the MNDO[10] and AM1[9] methods. All geometries were optimized without any assumptions. TSs were located by the reaction coordinate method,[11] refined by the gradient norm minimization[12] and characterized by confirming only one negative eigenvalue in the Hessian matrix.[13]

RESULTS AND DISCUSSION

Initial decomposition of acetic anhydride and diacetyl sulphide

Two major modes are conceivable for the pyrolysis of these diacetyl compounds: (i) elimination through the six-membered ring TS of the keto form, **1**, and (ii) that of the enol form, **2**, for which two more rotamer varieties, **4** and **5**, are possible. However, prior to the occurrence of these enolic TSs, transformation of the thermodynamically stable keto form into its enolic

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(2)
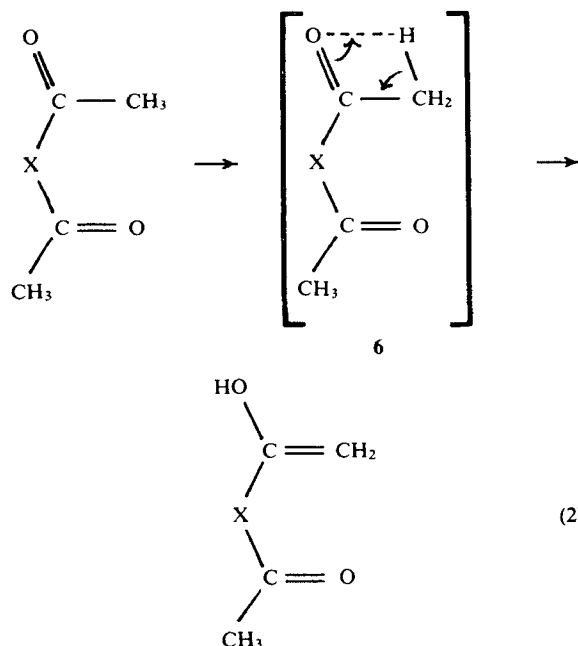
form [equation (2)] must precede; here a methyl hydrogen migrates in a 1,3-hydrogen rearrangement through a four-membered TS, **6**. Thus, all subsequent TSs involving the enol form, **2**, **4** and **5**, in the pyrolysis of the diacetyl compounds should depend on the activation barrier to this H-shift preceding them if they are to have any significance as a rate-determining step. We have compared the barrier heights (heats of activation, $\Delta H^{\ddagger}$) for the two processes through TSs **1** and **6** in Table 1. Three points of interest are apparent from this comparison: (i) both MNDO and AM1 predict that TS **1** is far more favourable than TS **6**, indicating that the pyrolysis of diacetyl compounds is unlikely to occur through the enolic TSs such as **2**, **4**, and **5**; (ii) diacetyl sulphide (X = S) has a lower barrier than acetyl anhydride (X = O) in all cases, i.e. the barrier is lower with X = S for TS **1** with both MNDO and AM1, which is in agreement with the trend reported by Blake and Speis[4]

Table 1. Heats of formation of ground (GS) and transition states (TS) in kcal mol^{-1} for the pyrolysis of $(CH_3CO)_2X$ with X = O and S.

Method	X		GS	TS 1	TS 6
MNDO	O	ΔH_f	$-132 \cdot 62$	$-59 \cdot 02$	$-32 \cdot 84$
		$\Delta H^{\ast}$		$73 \cdot 60$	$99 \cdot 78$
	S	ΔH_f	$-82 \cdot 07$	$-10 \cdot 16$	$16 \cdot 01$
		$\Delta H^{\ast}$		$71 \cdot 91$	$98 \cdot 08$
AM1	O	ΔH_f	$-131 \cdot 69$	$-79 \cdot 67$	$-45 \cdot 17$
		$\Delta H^{\ast}$		$52 \cdot 02$	$86 \cdot 52$
	S	ΔH_f	$-65 \cdot 08$	$-13 \cdot 86$	$17 \cdot 80$
		$\Delta H^{\ast}$		$51 \cdot 22$	$82 \cdot 88$

but conflicts with that by Taylor;[3] however, we must recognize that the differences in the theoretical barrier heights are very small indeed $(\Delta\Delta H^{\ast} = 0 \cdot 8$ kcal mol^{-1} by AM1), suggesting that the experimental activation energies may depend on the reaction conditions, e.g. temperature and surface catalysis;[4] and (iii) the calculated activation enthalpies are greater by ca 20 kcal mol^{-1} than the experimental values, and the MNDO barriers are uniformly higher than those of the AM1 values. These could result from underestimation of the hydrogen-bond energies in these semiempirical TS calculations; this is supported by the even higher barrier obtained with MNDO, since in this method the

hydrogen-bond energies are not accounted for[10] owing to an overestimation of repulsive interactions for species containing long bonds. Our recent work on water dimers and protonated water dimers indicated that the AM1 method also underestimates the hydrogen-bond energies.[14] The importance of hydrogen bonding in the TS is evident by large increases in positive charge at the β-hydrogen $(\Delta q > 0)$ and in the C_β—H bond length $(\Delta d > 0)$ in the activation process as shown in Table 2. It can be seen that the extension of C_β—H bond (C-5—H-6) during the activation process is larger by approximately a factor of two than that of the cleaving C_α—X bond (C-4—O-3 or C-4—S-3), especially with X = O, and accumulations of negative charge on C_β (C-5) and that of positive charge on β-hydrogen (H-6) far exceed those on O-3 and C-4. Hence it appears that the nucleophilic attack of the carbonyl group on the β-hydrogen is more advanced than the cleavage of the C_α—X bond in the TS, suggesting the importance of resonance 3, especially for X = O. The order of barrier height, X = S < X = O reflects, however, the ease of C_α—X bond breaking, since C_α—X bond breaking in the TS, Δd(C-4—X), is greater for X = S than for X = O, in agreement with the weaker bond energy for the C—S than C—O bond. The experimental rate order of the diacetyl compounds with varying X has been reported by Taylor[3] to be O > NH > S > CH$_2$, which is not in the order of increasing C_α—X bond strength,

Table 2. Formal charges (electronic units) and bond lengths (Å) in ground (GS) and transition states (TS) in the pyrolysis of $(CH_3CO)_2X$ through TS 1 by AM1

		Charge			Bond length			
X	Atom	GS	TS	Δq^a	Bond	GS	TS	Δd^a
O	O-1	$-0 \cdot 294$	$-0 \cdot 324$	$-0 \cdot 030$	O-3—C-4	$1 \cdot 385$	$1 \cdot 594$	$0 \cdot 209$
	C-2	$0 \cdot 325$	$0 \cdot 367$	$0 \cdot 042$	C-5—H-6	$1 \cdot 118$	$1 \cdot 610$	$0 \cdot 492$
	O-3	$-0 \cdot 331$	$-0 \cdot 321$	$0 \cdot 010$	C-4—H-5	$1 \cdot 488$	$1 \cdot 385$	$-0 \cdot 103$
	C-4	$0 \cdot 326$	$0 \cdot 384$	$0 \cdot 058$	O-3—C-2	$1 \cdot 385$	$1 \cdot 296$	$-0 \cdot 089$
	C-5	$-0 \cdot 221$	$-0 \cdot 625$	$-0 \cdot 404$	O-1—C-2	$1 \cdot 225$	$1 \cdot 305$	$0 \cdot 080$
	H-6	$0 \cdot 120$	$0 \cdot 350$	$0 \cdot 230$				
S	O-1	$-0 \cdot 246$	$-0 \cdot 274$	$-0 \cdot 028$	S-3—C-4	$1 \cdot 721$	$1 \cdot 998$	$0 \cdot 277$
	C-2	$0 \cdot 124$	$0 \cdot 081$	$-0 \cdot 043$	C-5—H-6	$1 \cdot 118$	$1 \cdot 605$	$0 \cdot 487$
	S-3	$0 \cdot 058$	$0 \cdot 015$	$-0 \cdot 043$	C-4—C-5	$1 \cdot 491$	$1 \cdot 378$	$-0 \cdot 113$
	C-4	$0 \cdot 124$	$0 \cdot 296$	$0 \cdot 172$	S-3—C-2	$1 \cdot 721$	$1 \cdot 619$	$-0 \cdot 102$
	C-5	$-0 \cdot 246$	$-0 \cdot 624$	$-0 \cdot 378$	O-1—C-2	$1 \cdot 229$	$1 \cdot 312$	$0 \cdot 083$
	H-6	$0 \cdot 115$	$0 \cdot 340$	$0 \cdot 225$				

$^a \Delta q$ and Δd are the changes in charge and bond length, respectively, in the activation process through TS 1.

Table 3. Heats of formation, ΔH_f, of ground states (GS), intermediates (IM) and transition states (TS), and activation enthalpies (ΔH^*) in $kcal\,mol^{-1}$

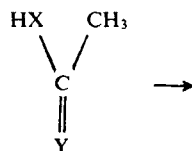| Method	Reactant	Parameter	GS	TS (tautom.)	TS A	TS B	TS C	TS D	IM	TS D₁	TS D₂
MNDO	HSCCH₃ ‖ O	ΔH_f	−41·40	22·49	54·79	48·97	86·97	55·52	−32·45	56·93	38·10
		ΔH^*		63·89	96·19	90·37	128·37	96·92		98·33	79·50
	HOCCH₃ ‖ S	ΔH_f	−37·32	22·49	78·73	63·18	108·97	36·31	−32·45	38·10	56·93
		ΔH^*		59·81	116·05	100·50	146·29	73·63		75·42	94·25
AM1	HSCCH₃ ‖ O	ΔH_f	−34·47	14·97	59·17	33·75	73·65	47·42	−23·18	41·47	32·24
		ΔH^*		49·44	93·64	68·22	108·12	81·89		75·94	66·71
	HOCCH₂ ‖ S	ΔH_f	−25·03	14·97	76·85	54·52	63·87	35·78	−23·18	32·24	41·47
		ΔH^*		40·00	101·88	79·55	88·90	60·81		57·27	66·50
	HOCCH₃ ‖ O	ΔH_f	−103·02	−52·10	−6·75	−20·22	16·10	−17·20	−83·02	−23·77	−23·77
		ΔH^*		50·92	96·27	82·20	119·12	85·82		79·23	79·23

C—N < C—S < C—O < C—C (standard bond energies are[15] C—C 83·2, C—O 81, C—S 71, C—N 69·7 $kcal\,mol^{-1}$), but shows that the overall reactivity is determined by the ease of both C_α—X bond cleavage and nucleophilic attack on the β-hydrogen.

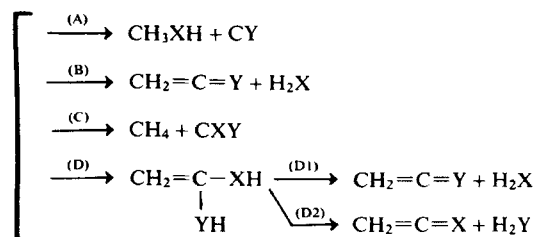## Pyrolysis of acetic and thioacetic acids

Acetic and thioacetic acids are by-products of the thermal decomposition of acetic anhydride and diacetyl sulphide, respectively. These undergo further elimination to various products. Experimentally it has been shown that the initial form of thioacetic acid is the thiono- form, which rapidly equilibrates to the more stable thiolo- form at high temperature.

The results in Table 3 show that both MNDO and AM1 predict the thiolo- form to be the more stable tautomer, and the AM1 barrier height to the tautomerization is $49\cdot4\,kcal\,mol^{-1}$, the MNDO barrier being even higher, $\Delta H^* = 63\cdot9\,kcal\,mol^{-1}$.

Four modes of pyrolysis are possible for acetic and thioacetic acid (Scheme 1): (A) alcohol formation, (B) ketene formation, (C) methane formation and (D) diol formation, followed by further elimination to ketene. Heats of formation of the products are given in Table 4, and those of equilibrium species and activation barriers (ΔH^*) involved in each modes of pyrolysis are summarized in Table 3. For acetic acid, tautomerization requires a higher activation enthalpy than for thioacetic acid, and ketene formation (B) provides the lowest barrier path. The initial step in process (D) is a 1,3-hydrogen shift, which has a slightly (ca 3 $kcal\,mol^{-1}$) higher barrier than process (B). Two subsequent processes of ketene formation, (D₁) and (D₂), in this case (X = Y = O), are indistinguishable. Both processes (A) and (C) have a higher activation enthalpy than (B), so that methane formation is unfavourable compared with
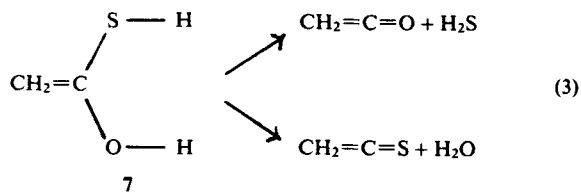
(X, Y = O or S)

(A) → CH₃XH + CY

(B) → CH₂=C=Y + H₂X

(C) → CH₄ + CXY

(D) → CH₂=C—XH →(D1) CH₂=C=Y + H₂X
             | \→(D2) CH₂=C=X + H₂Y
            YH

Scheme 1

Table 4. Heats of formation of products in $kcal\,mol^{-1}$

| Product	MNDO	AM1
H₂S	3·83	3·99
CH₂CO	−6·80	−5·66
CH₄	−11·95	−8·78
COS	−22·89	−13·71
CH₃SH	−7·28	−3·35
CO	−5·92	−5·68
CH₃OH	−57·35	−57·03
H₂O	−60·94	−59·24
CH₂CS	48·54	54·23
CS	104·56	99·86
CO₂	−75·08	−79·83

the ketene formation, which is in accord with the experimental results.[3]

For the thioacetic acid decomposition, we considered all four processes, (A)–(D), from both the thiono- and thiolo- forms. In the decomposition of the more stable thiolo- form, the ketene formation (B) again provides the lowest reaction path, other processes having substantially higher activation barriers. In the case of the thiono- form, elimination through (D) is the most favoured. However, both MNDO and AM1 predict that once the intermediate diol 7 is formed, the ketene formation is always preferred to the thioketene formation both kinetically and thermodynamically [equation (3)]:

$$
\begin{array}{c}
\underset{\displaystyle CH_2=C}{\overset{\displaystyle S\!-\!H}{\diagup}} \quad \underset{\displaystyle CH_2=C=S + H_2O}{\overset{\displaystyle CH_2=C=O + H_2S}{}} \\
\underset{\displaystyle O\!-\!H}{\diagdown}
\end{array}
\qquad (3)
$$

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This is in apparent contradiction to the experimental results that thioketenes[16] are not found. However this process starting from the unstable thiono- form may not occur under the experimental conditions.

When R is varied in 8 the experimental reactivity of the ketene formation (B) was in the order $SH > NH_2 > OH$.[17] This order of reactivity, which is reproduced with AM1 but not with MNDO as shown in Table 5, can be readily rationalized: breaking of the C_α—X bond is the most important step of the reaction for R = SH, **9**, whereas for R = OH this factor is relatively unimportant compared with the nucleophilic attack on the β-hydrogen, **10**, which may also be


8   **9**   **10**
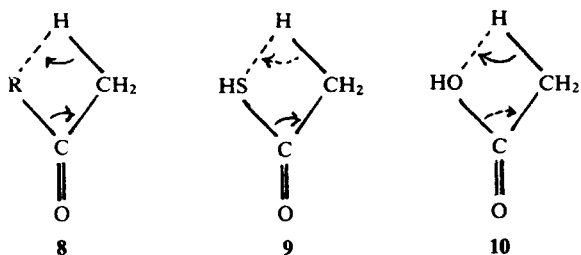
enhanced by resonance similar to 3. This rationalization of the reactivity order is supported by the changes in electron density and bond length accompanied by the activation process shown in Table 6. Examination of Table 6 reveals that the extent of bond cleavage, Δd (C-2—H-3), and positive charge development on β-hydrogen, Δq(H-3), is the greatest with X = O and the least with X = S, whereas the C_α—X bond cleavage, Δd(C-1—X-4), is the greatest with X = S and the least

Table 5. Heats of formation, ΔH_f, of ground (GS) and transition states (TS) and activation enthalpies (ΔH^*) in kcal mol^{-1} for the pyrolysis of $RCOCH_3$ with R = SH, NH_2 and OH through paths (B) and (C)

Method		SH	NH_2	OH
MNDO	ΔH_f, GS	$-41\cdot41$	$-46\cdot81$	$-101\cdot11$
	ΔH_f, TS(B)	$48\cdot97$	$36\cdot22$	$-1\cdot71$
	$\Delta H_B^{\ddagger}$	$90\cdot38$	$83\cdot03$	$99\cdot40$
AM1	ΔH_f, GS	$-34\cdot47$	$-50\cdot69$	$-103\cdot02$
	ΔH_f, TS(B)	$33\cdot75$	$26\cdot11$	$-20\cdot22$
	$\Delta H_B^{\ddagger}$	$68\cdot22$	$76\cdot80$	$82\cdot80$
	ΔH_f, TS(C)	$73\cdot65$	$67\cdot02$	$16\cdot10$
	$\Delta H_C^{\ddagger}$	$108\cdot12$	$117\cdot71$	$119\cdot12$

with X = O. This clearly indicates that although the overall reactivity is determined by a balance of the two factors, the ease of C_α—X bond cleavage is relatively more important than nucleophilic attack on the β-hydrogen, which is consistent with the trend found above in the initial decomposition of diacetyl series with X = O and S. It is interesting that the reactivity order for methane formation (C) is same as that for ketene formation (B). This order of reactivity for process (C) is, however, dependent on an entirely different factor, viz. the order of the X—H bond energy, which is O—H > N—H > S—H (Standard bond energies are[15] O—H $111\cdot8$, N—H $93\cdot4$, S—H $87\cdot8$ kcal mol^{-1}). In this process, the difference in the X—H bond energy should be the only factor in determining the ease of the four-centre TS formation with X = O, NH and S, **11**.

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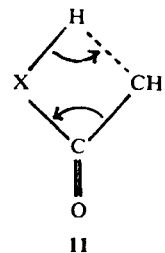
We therefore conclude that the ketene formation constitutes the major process in the initial decomposition of diacetyl compounds, **1**, and also in the subsequent pyrolysis of acetic and thioacetic acids, and in these pyrolysis both the ease of C_α—X bond breaking (for X = S) and nucleophilic attack on the β-hydrogen (for X = O) are important in determining the overall relative reactivity. In the methane formation process, however, the reactivity order is entirely dependent on the bond strength of the X—H bond for X = O, NH and S. Both AM1 and MNDO tend to overestimate the activation barriers, probably because they do not take proper account of hydrogen bonding energies in the TS, especially in the latter method.

Table 6. Formal charges (electronic units) and bond lengths (Å) in ground (GS) and transition states (TS) for the pyrolysis of $RCOCH_3$ (R = SH, NH_2 or OH) through the ketene formation path, (B), by AM1
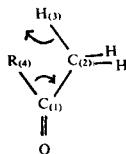
R	Atom	Charge			Bond length			
		GS	TS	Δq^a	Bond	GS	TS	Δd^a
SH	C-1	0·115	0·419	0·304	C-1—S-4	1·703	2·266	0·563
	C-2	−0·253	−0·546	−0·293	C-2—H-3	1·118	1·471	0·353
	H-3	0·116	0·286	0·170	C-1—C-2	1·489	1·384	−0·105
	S-4	0·032	−0·415	−0·447	H-3—S-4	2·913	1·548	−1·365
NH_2	C-1	0·300	0·344	0·044	C-1—N-4	1·375	1·528	0·153
	C-2	−0·242	−0·664	−0·422	C-2—H-3	1·117	1·636	0·519
	H-3	0·118	0·311	0·193	C-1—C-2	1·508	1·433	−0·075
	N-4	−0·443	−0·303	0·140	H-3—N-4	2·793	1·214	−1·579
OH	C-1	0·306	0·398	0·092	C-1—O-4	1·364	1·492	0·128
	C-2	−0·217	−0·556	−0·339	C-2—H-3	1·117	1·709	0·592
	H-3	0·117	0·311	0·194	C-1—C-2	1·486	1·412	−0·074
	O-4	−0·321	−0·384	−0·063	H-3—O-4	2·675	1·142	−1·533

$^a \Delta q$ and Δd are the changes involved in charge and bond length, respectively, during the activation process through path (B).

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