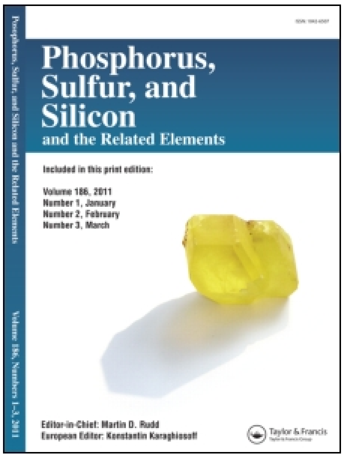

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# Ab Initio and NBO Studies of the Decomposition ([2 2] and [2 4]Elimination) Mechanisms of Alkyl*iso*thiocyanates (alkyl = ethyl-, *iso*-propyl- and *tert*-butyl)

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# Ab Initio and NBO Studies of the Decomposition ([2+2] and [2+4]Elimination) Mechanisms of Alkyl*iso*thiocyanates (alkyl = ethyl-, *iso*-propyl- and *tert*-butyl)

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*Ab initio Molecular Orbital (MO), Density Functional Theory (DFT), and Natural Bond Orbital (NBO) population analysis were used to investigate the mechanism of the decomposition of ethyl*iso*thiocyanate (**1**),* iso*-propyl*iso*thiocyanate (**2**), and* tert*-buthyl*iso*thicyanate (**3**). HF/6-31G**//HF/6-31G** and B3LYP/6-31G**//HF/6-31G** results indicate that for the decomposition of compounds **1–3**, the six-membered transition state structures via concerted [2+4]elimination mechanisms have lower energies than the four-membered transition state geometries via [2+2]eliminations. The results at B3LYP/6-31G**//HF/6-31G** and HF/6-31G**//HF/6-31G** levels of theory revealed that the barrier height for the decomposition of compound **1**, through the six-membered transition state structure via the concerted [2+4] elimination mechanism, is 46.31 kcal mol$^{-1}$ and 59.51 kcal mol$^{-1}$, while the barrier height for the four-membered transition state structure via [2+2] elimination is 71.06 kcal mol$^{-1}$ and 72.09 kcal mol$^{-1}$, respectively.*

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*[2+4]elimination mechanism by B3LYP/6-31G**//HF/6-31G** method (46.31 kcal mol$^{-1}$) is in a good agreement with the reported experimental results (45.35 kcal mol$^{-1}$). The obtained barrier heights* via *the [2+4]elimination mechanism at the B3LYP/6-31G**//HF/6-31G** and HF/6-31G**//HF/6-31G** levels of theory show also that the decomposition energy barriers via the [2+4]elimination mechanism for compound **1–3** are in the following order: **1** > **2** > **3**. The obtained order of energy barriers could be explained by the number of electron-releasing methyl groups substituted to the $C_{sp3}$ atom (which is attached to the N atom). NBO analysis shows that the occupancies of $\sigma_{Csp3\text{-}N}$ bonds decrease in the following order: **3** < **2** < **1** and the occupancies of $\sigma^*_{Csp3\text{-}N}$ bonds increase in the opposite order. This fact illustrates a comparatively easier unsymmetrical dissociation of the $\sigma_{Csp3\text{-}N}$ bond in compound **3** compared to compound **2**, and in compound **2** compared to compound **1**.*

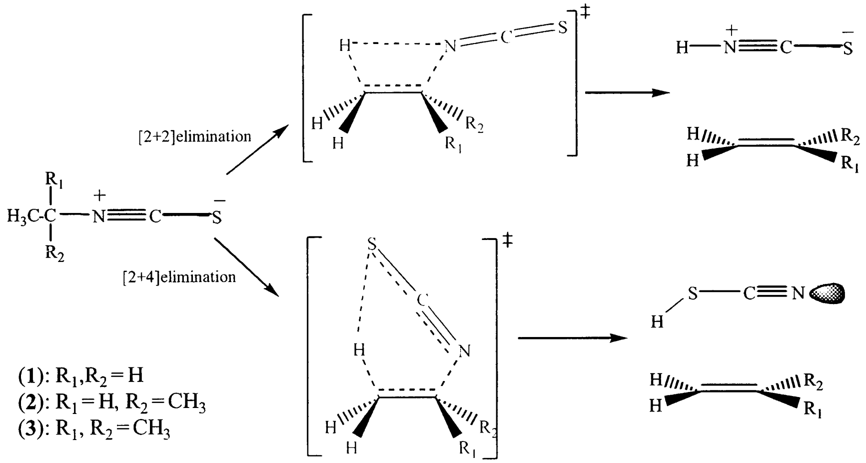
**Keywords** *Iso*thiocyanate; decomposition; molecular modeling; ab initio; natural bond orbital

## INTRODUCTION

The experimental study of the kinetic of pyrolysis of *iso*thiocyanate compounds, investigated by Barroeta and Maccoll,[1] showed that the decomposition reaction is a unimolecular process. However, they were not able to define clearly which of the two product tautomeric forms (thiocyanic acid or *iso*thiocyanic acid) is produced by the pyrolysis process of ethyl*iso*thiocyanate (**1**), *iso*-propyl*iso*thiocyanate (**2**), and *tert*-buthyl*iso*thicyanate (**3**). They were inclined to believe in a four-centered transition state structure, in which a nitrogen–hydrogen interaction takes place by way of the unpaired sp$^2$ electrons in the former atom. Barroeta and Umana[2] have studied the transition-state structure for the pyrolysis of ethyl*iso*thiocyanate by the activation entropy and frequency factor calculations. Their results supported a six-membered transition state rather than a four-membered transition state structures.

Although, Schnider and Rabinoviotch have suggested a polar transition state structure for the pyrolysis of ethyl*iso*thiocyanide,[3] Casanova and colleagues[4] have presented evidence, which is contrary to this suggestion.

The successful application of density functional theory (DFT) based methods have broadened the applicability of the computational methods and now represents an interesting approach for determining activation barrier and molecular energies.[5–9] The B3LYP method combines Becke's three-parameter exchange function with the correlation function of Lee and colleagues.[6,7] Therefore, in this work, ab initio molecular orbital (MO),[5] DFT (B3LYP) methods[6–9] and NBO analysis[10–13] were performed for the investigation of the pyrolysis reactions of ethyl*iso*thiocyanate (**1**), *iso*propyl*iso*thiocyanate (**2**), and *tert*-butyl*iso*thiocyanate (**3**), and also for addressing, particularly, the arisen questions about these reactions (see Scheme 1).



**SCHEME 1**

## CALCULATIONS

Ab initio calculations were carried out using HF/6-31G**//HF/6-31G** and B3LYP/6-31G**//HF/6-31G** levels of theory with the GAUSSIAN 98 package programs[5] implemented on a Pentium-PC computer with a 550 MHz processor. Initial structural geometries of compounds **1–3** were obtained by a molecular mechanic program PCMODEL (88.0)[14] and for future reoptimization of geometries, the AM1 method of a MOPAC 6.0 computer program was used.[15] Energy minimum geometries were located by minimizing energy, with respect to all geometrical coordinates without imposing any symmetrical constraints.

The GAUSSIAN 98 program finally was used to perform ab initio calculations at the HF/6-31G** level in order to obtain the energy minimum structures and B3LYP/6-31G**//HF/6-31G** levels for single-point energy calculations.

The nature of the stationary points for compounds **1–3** has been fixed by means of the number of imaginary frequencies. For minimum state structures, only real frequency values, and in the transition state, only a single imaginary frequency value, was accepted.[16]

The structure of the molecular transition-state geometries was located by using the optimized geometries of the equilibrium molecular structure, according to the procedure of Dewar and colleagues (keyword

**TABLE I Calculated Total Energies *E*, *ZPE*, and Relative Energies $\Delta E_0$ ($E_h$, in Hartree) for Ground and Transition States of the Thermal Decomposition of Compounds 1–3**

| Method | | HF/6-31G**// HF/6-31G** | | | B3LYP/6-31G**// HF/6-31G** | | | |
|---|---|---|---|---|---|---|---|---|
| system | *ZPE* | $E_{el}$ | $E_0$ | $\Delta E_0$[a] | $E_{el}$ | $E_0$ | $\Delta E_0$[a] | Exp. |
| **1** (GS) | 0.082328 | −568.476997 | −568.394669 | 0.000000<br>(0.000000)[b] | −570.270194 | −570.187866 | 0.000000<br>(0.000000)[b] | |
| **1** (TS, [2+2]) | 0.074501 | −568.354289 | −568.279788 | 0.114881<br>(72.088976) | −570.149122 | −570.074621 | 0.113245<br>(71.062370) | |
| **1**(TS, [2+4]) | 0.073266 | −568.373092 | −568.299826 | 0.094843<br>(59.514931) | −570.187325 | −570.114059 | 0.073807<br>(46.314631) | (45.35)[c] |
| **2** (GS) | 0.112169 | −607.518540 | −607.518254 | 0.000000<br>(0.000000) | −609.589973 | −609.477804 | 0.000000<br>(0.000000) | |
| **2** (TS, [2+2]) | 0.102102 | −607.416462 | −607.314360 | 0.091725<br>(57.558355) | −609.510054 | −609.407952 | 0.69852<br>(43.832828) | |
| **2** (TS, [2+4]) | 0.102597 | −607.423982 | −607.321385 | 0.084700<br>(53.150097) | −609.513790 | −609.411193 | 0.066611<br>(41.799069) | (42.87)[c] |
| **3** (GS) | 0.141627 | −646.558329 | −646.416702 | 0.000000<br>(0.000000) | −648.908668 | −648.767041 | 0.000000<br>(0.000000) | |
| **3** (TS, [2+2]) | 0.132185 | −646.468479 | −646.336294 | 0.080408<br>(50.456824) | −648.827052 | −648.694867 | 0.072174<br>(45.289907) | |
| **3** (TS, [2+4]) | 0.1312674 | −646.472634 | −646.34.960 | 0.075742<br>(47.528862) | −648.839165 | −648.707491 | 0.059550<br>(37.368220) | (39.46)[c] |

[a] Relative to the ground state structure.

[b] Numbers in parenthesis are the corresponding $\Delta E_0$values in kcal $mol^{-1}$.

[c] Experimental data [see ref. 1].

SADDLE).[17] These structures were then reoptimized by the QST2 option at the HF/6-31G** level. The vibrational frequencies of ground and transition states were calculated by FREQ subroutine.

## RESULTS AND DISCUSSION

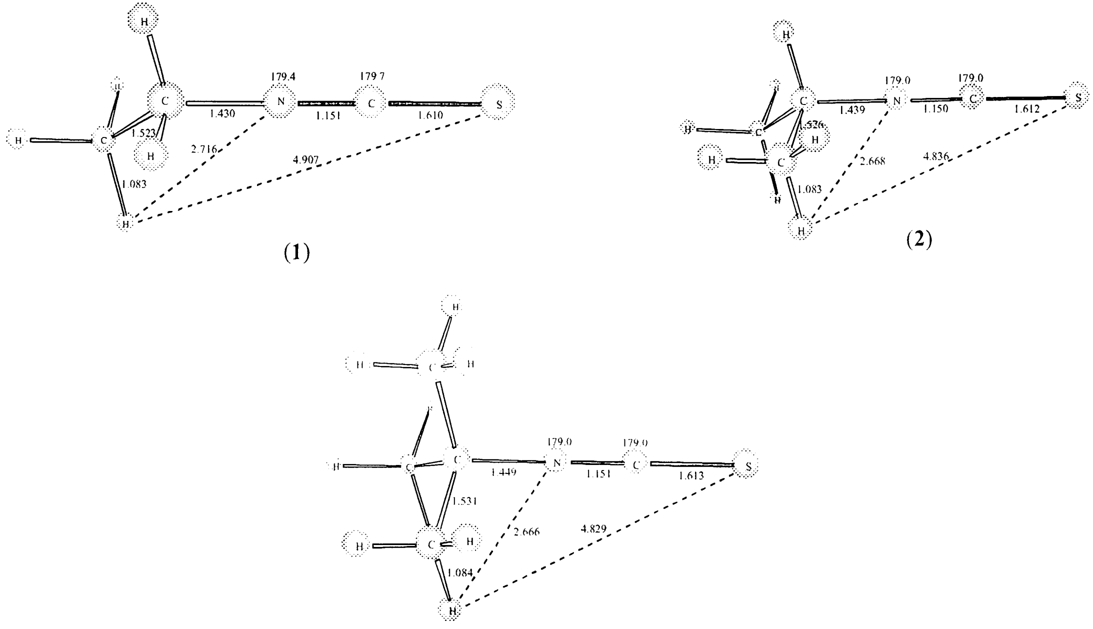
Zero point (*ZPE*) and total electronic ($E_{\text{el}}$) energies ($E_0 = ZPE + E_{\text{el}}$) for ground- and transition-state structures of the [2+2] and [2+4]elimination reactions for compounds **1–3**, as calculated by the ab initio HF/6-31G** level of theory, are given in Table I. The DFT-based method (B3LYP/6-31G**//HF/6-31G**) was used for single-point energy calculations.

According to the B3LYP/6-31G**//HF/6-31G** calculation, the energy barriers for decomposition of compounds **1–3**, via six-membered transition state structures ([2+4]eliminations), to the related alkenes and thiocyanic acid products are 46.31, 41.80, and 37.37 kcal mol$^{-1}$, respectively. These energy barriers via four-membered transition state structures ([2+2]eliminations) to the related alkenes and *iso*thiocyanic acid products are 71.06, 43.83, and 45.29 kcal mol$^{-1}$, respectively, as calculated by the same level of theory (see Table I).

The calculated results show that the decomposition of compounds **1–3** via six-membered transition state structures ([2+4]elimination) require lower activation energy barriers compared to the four-membered transition state structures ([2+2]eliminations). Accordingly, based on these calculations, the corresponding decomposition reactions should proceed via [2+4]elimination paths. The obtained energy barriers for [2+4]elimination paths also are in good agreement with the previously reported experimental data (see Table I).

The decomposition energy barriers via the [2+4]elimination mechanism for compounds **1–3** are in the following order: **1** > **2** > **3**, as calculated by both B3LYP/6-31G**//HF/6-31G** and HF/6-31G**//HF/6-31G** levels of theory. This trend can be explained by the number of electron-releasing methyl groups substituted to the $C_{\text{sp3}}$ atom (which is attached to the N atom).

NBO analysis shows also that the increase of the number of the attached methyl groups to the $C_{\text{sp3}}$ atom (which is attached to the N atom) of the occupancies of $\sigma_{\text{Csp3-N}}$ bonds decrease in the following order: **3** < **2** < **1**. The occupancies of $\sigma^*_{\text{Csp3-N}}$ bonds increase in a parallel manner in the opposite order (see Table II). This fact illustrates the easier unsymmetrical dissociation of the $\sigma_{\text{Csp3-N}}$ bond in compound **3** (and also its relatively lowest energy barrier) compared to compound **2**, and in compound **2**, the dissociation was easier than in compound **1**.

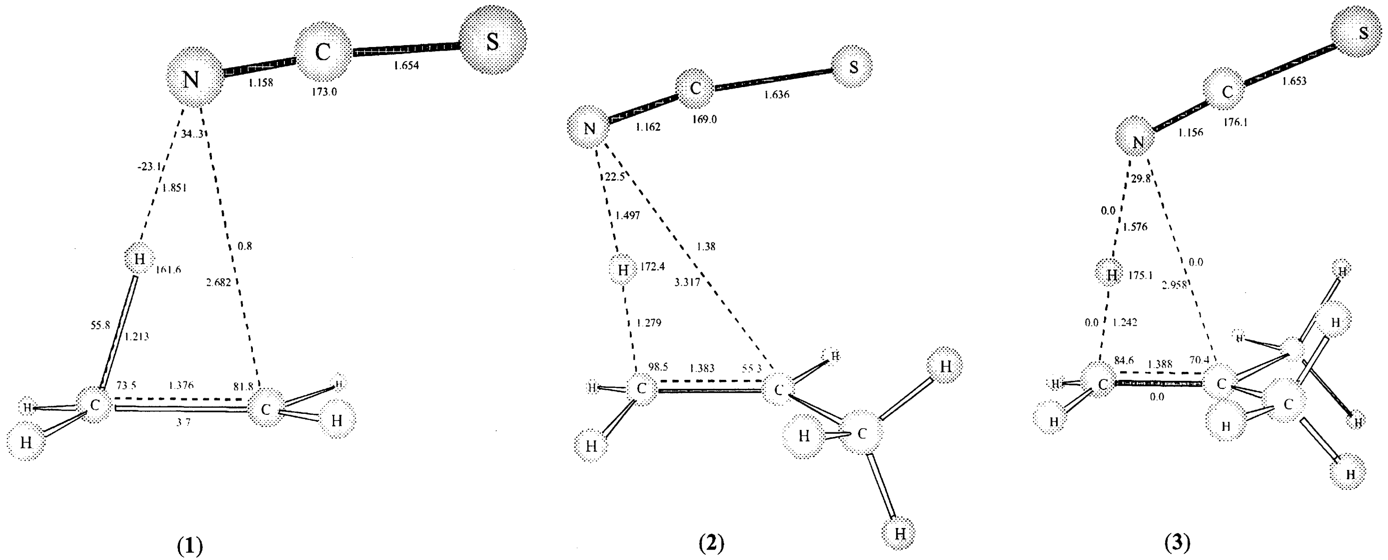


(1)

(2)

(3)

**FIGURE 1** HF/6-31G**-calculated structural parameters for the ground-state structures of compounds**1–3**. Bond lengths are in angström (Å) unit and angles in degrees (°C).

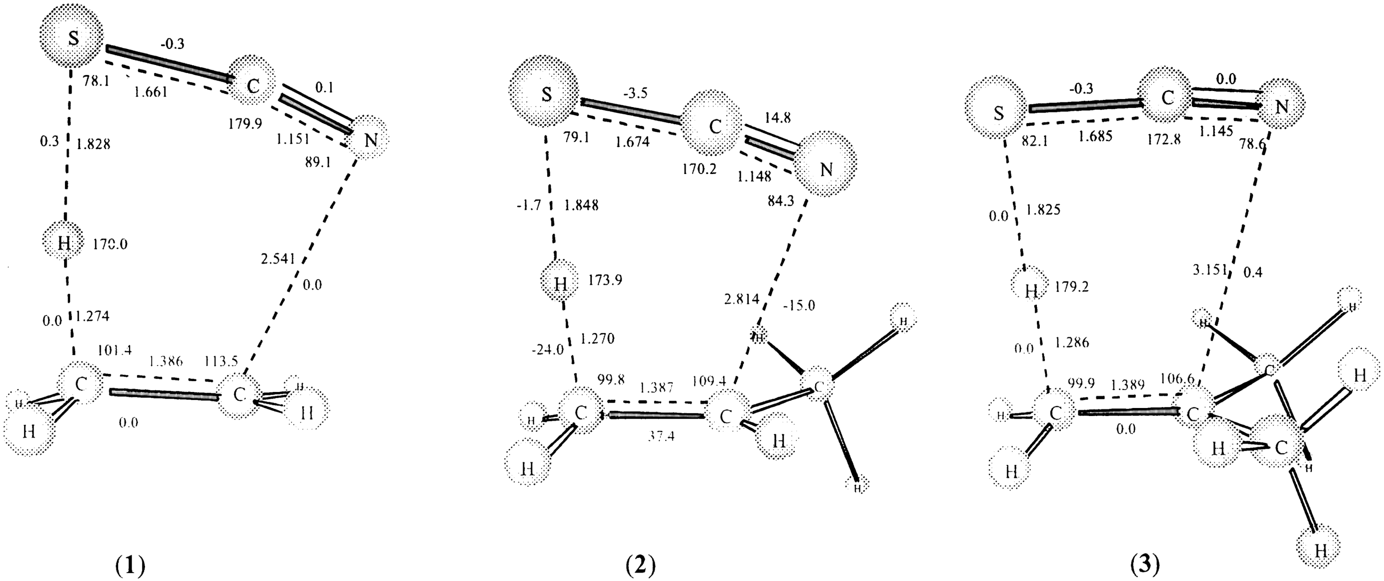


(1)

(2)

(3)

**FIGURE 2** HF/6-31G**-calculated structural parameters for the four-membered transition-state structures of compounds **1–3**. Bond lengths are in angstrom (Å) unit and angles in degrees (°C).



(1) (2) (3)

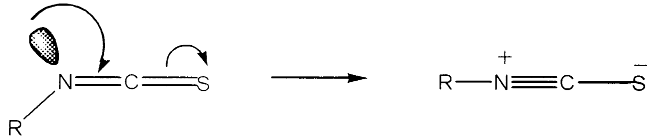
**FIGURE 3** HF/6-31G**-calculated structural parameters for the six-membered transition-state structures of compounds **1–3**. Bond lengths are in angstrom (Å) unit and angles in degrees (°C).

**TABLE II NBO-Calculated Occupancies of $\sigma_{Csp3\text{-}N}$ Bonding and $\sigma^*_{Csp3\text{-}N}$ Antibonding Orbitals for Compounds 1–3**

| | compound | | |
|---|---|---|---|
| bond | **1** | **2** | **3** |
| $\sigma_{Csp3\text{-}N}$ | 1.98655 | 1.98308 | 1.97935 |
| $\sigma^*{}_{Csp3\text{-}N}$ | 0.02029 | 0.03130 | 0.04232 |

Representative structural parameters for ground and transition state structures, as calculated by the HF/6-31G** level of theory, are shown in Figures 1–3. It is known that theoretical calculations provide structural parameters for isolated molecules at 0 K, which are not reported, in principle, to reproduce quantitatively the experimental values.[17] Nevertheless, it is possible to carry out ab initio calculations at the Hartree-Fock level, from which many properties and structures can be obtained with an accuracy that is competitive with experiments.[18–22]

HF/6-31G** results show that compounds **1–3** have linear structure (see Scheme 2 and Figure 1). Also, HF/6-31G**-calculated structural parameters show that the angle strain in the [2+4]elimination transition-state structure is greater than in the [2+4]elimination reaction (see Figures 2–3). This fact could explain the higher-barrier energy for the [2+2]elimination compared to the [2+2]elimination.



**SCHEME 2**

## CONCLUSION

Ab initio and DFT calculations performed in this article provided a picture from both structural, energetic, and mechanistic points of view for compounds **1–3**. HF/6-31G**//HF/6-31G** and B3LYP/6-31G**//HF/6-31G** results indicated that, for the decomposition of compounds **1–3**, the six-membered transition state structures via the concerted [2+4]elimination mechanism is energetically more favorable than the four-membered transition-state geometries via the [2+2]elimination. The decomposition barrier heights via the [2+4]elimination mechanism for compounds **1–3** are in the following order: **1** > **2** > **3**, as calculated by the B3LYP/6-31G**//HF/6-31G** and HF/6-31G**//HF/6-31G** levels of theory.

The resulted order of barrier heights could be explained by the number of electron-releasing methyl groups substituted to the $C_{sp3}$ atom (attached to the N atom), as confirmed by the NBO analysis. Effectively, the NBO analysis shows that the occupancies of $\sigma_{Csp3-N}$ bonds decrease for compounds **1–3** as **3** < **2** < **1**, and the occupancies of $\sigma^*{}_{Csp3-N}$ bonds increase in the opposite order. This fact illustrates the easier unsymmetrical dissociation of the $\sigma_{Csp3-N}$ bond in compound **3** compared to compound **2**, and also the easier unsymmetrical dissociation in compound **2**, compared to compound **1**.

Finally, it can be seen that from a thermodynamical point of view, thiocyanic acid generally is more stable than *iso*thiocyanic acid, and from a kinetical point of view, the [2+4]elimination mechanisms (with lower barrier heights) are preferred to the [2+2]elimination mechanisms. In conclusion, from both thermodynamic and kinetic points of view, the [2+4]elimination mechanism should be considered as the preferred mechanism in the thermal decomposition of compounds **1–3**.

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