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# Experimental and Theoretical Studies on the Isomerization of Allyl Thiocyanate to Allyl Isothiocyanate

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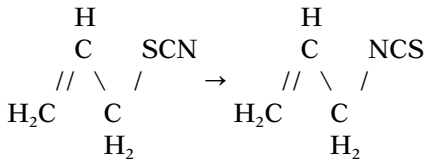
## ABSTRACT

*The mechanism of isomerization of allyl thiocyanate to allyl isothiocyanate has been investigated both experimentally and theoretically. The kinetic study indicates that the reaction is unimolecular and is not ionic. The entropy of activation suggests strongly that the mechanism involves a cyclic transition state. The rate of reaction was retarded to a small extent in polar solvents relative to that in nonpolar solvents. Ab initio MO calculations indicate, in agreement with the experimental results, that the reaction proceeds through a cyclic transition state, one in which the SCN moiety is almost linear. Thus, this is a [3,3] sigmatropic rearrangement. The charge separation in the transition state was substantial. The retardation of the reaction in polar solvents was attributed to the difference in solvation in the original state and in the transition state.* © *1997 John Wiley & Sons, Inc.*

## *INTRODUCTION*

The rearrangement of an organic thiocyanate to the corresponding isothiocyanate is a well-known process. As early as 1925, Biller reported the isomerization of allyl thiocyanate to allyl isothiocyanate [1]. The isomerization was applied to the 1,3-butadienyl system [2] and was used for synthesis of a macrocyclic antibiotic [3]. However, the mechanism of the isomerization remained, at best, controversial.



While Biller had already invoked a cyclic mechanism in 1925 without any supporting evidence, this mechanism attracted the interest of many investigators. Mumm and Richter used this concept to explain the formation of a 1-substituted allyl isothiocyanate from a 3-substituted allyl thiocyanate [4]. Fava also favored the cyclic mechanism from a general point of view prevalent in organic chemistry [5]. Others invoked a more recent concept, viz., a "[3,3] sigmatropic shift" for this type of isomerization [6,7]. However, so far, a firm basis for the postulation has been lacking.

In fact, there are some reports that present experimental evidence opposing the cyclic mechanism. Iliceto et al. measured the rates of isomerization of allyl thiocyanates carrying a methyl group at the 1, 2, or 3 position and found that the rates are affected

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by the methyl substitution. In addition, they showed that there were solvent effects on the rates, polar solvents disfavoring the rearrangement to a small extent [8]. Although this may imply that the reaction is not ionic, the unusual solvent effects cannot be explained only by a simple consideration of a [3,3] sigmatropic rearrangement.

As to mechanisms other than the cyclic one, Smith and Emerson suggested an $S_N1$ type of reaction, as well as a reaction passing through an intermediate that consists of the alkyl cation coordinated to the thiocyano group of another molecule, and they also suggested formation of a six-membered and a four-membered cyclic transition state (TS) [9]. Iliceto et al. also invoked an equilibrium involving ionic intermediates for the isomerization [10].

It is also worthwhile to mention exceptions to occurrence of the reaction such that cinnamyl thiocyanate is known not to isomerize to the isothiocyanate [11,12] and furfuryl thiocyanate also fails to isomerize under various conditions [13].

Theoretical investigations should shed light on the details of the molecular mechanism of the isomerization. However, to the best knowledge of the present authors, there have been only a few attempts to provide theoretical considerations on the isomerization of allyl thiocyanate to isothiocyanate, although there are some reports that evaluate ionic substitution reactions of alkyl thiocyanates by the thiocyanate anion by use of the extended Hückel method [14] and by ab initio molecular orbital (MO) calculations [15].

In this article, we wish to present not only results of detailed kinetic studies involving solvent effects but also results obtained by ab initio MO calculations on the cyclic mechanism that can explain the experimental results in a reasonable manner. Both six-membered and four-membered transition states were considered that demonstrated the latter TS to be energetically disfavored.

## *RESULTS AND DISCUSSION*

### *Experimental Data Concerning the Nature of the Reaction*

Irrespective of the wealth of the literature, there are not many reports that explicitly consider the order of the reaction. Although Emerson and Titus [7] assumed that the reaction is first order in the substrate, we have thoroughly investigated this point by changing the concentration of the substrate and adding tetrabutylammonium thiocyanate. The results are shown in Table 1. All the kinetic data show that the reaction is indeed first order in the substrate and that additives do not affect the reaction rates. As a result, it is concluded that the reaction cannot be of the $S_N2$ type but is unimolecular. Solvent effects on kinetic parameters of the isomerization are compiled in Table 2. These data show that the kinetic parameters are hardly affected by the solvent polarity. The main feature of the kinetic parameters is a large negative entropy of activation, which might be taken as an indication of a cyclic mechanism.

**TABLE 1** Rates of Reaction at Various Concentrations in the Presence and Absence of the Additive

| *Allyl Thiocyanate* (*mol/L*) | *Tetra-n-butyl Ammonium Thiocyanate* (*mol/L*) | *Rate constant* ($\times 10^{-4}\ s^{-1}$) |
|---|---|---|
| 0.2 | 0.0 | 1.91 ± 0.08 |
| 0.2 | 0.05 | 1.86 ± 0.10 |
| 0.2 | 0.1 | 2.05 ± 0.08 |
| 0.2 | 0.2 | 1.99 ± 0.07 |
| 0.2 | 0.4 | 1.69 ± 0.10 |
| 0.2 | 0.8 | 2.09 ± 0.08 |
| 0.8 | 0.2 | 2.15 ± 0.03 |
| 0.4 | 0.2 | 1.80 ± 0.10 |
| 0.2 | 0.2 | 1.91 ± 0.09 |
| 0.1 | 0.2 | 1.99 ± 0.03 |

Reaction temperature was 80°C, and toluene was used as the solvent.

However, the rate constants of isomerization, which reflect small energy differences more clearly than do free energies of activation themselves, depend clearly on the solvent polarity, as shown in Figure 1 and Table 3. The most intriguing point is that the rates are diminished, rather than enhanced, in polar solvents in comparison to those determined by use of less polar solvents. This observation is in good agreement with the results of Iliceto et al. [8] and might be taken as a reflection of strong solvation of the reactant state relative to the TS of isomerization, although a straightforward explanation has not evolved from these data only. In order to shed light on these points, we have carried out ab initio MO calculations to complement the experimental results.

*Ab initio MO Calculations.* First of all, we have optimized the reactant state (RS) (allyl thiocyanate) and the product state (PS) (allyl isothiocyanate) for four levels of calculations. The optimized parameters for the most stable conformations are shown in Tables 4 and 5. Perspective views of these species are also given in Figure 2. The structures calculated by different methods do not differ significantly from one another, especially those resulting from ab initio MO calculations. In agreement with the experimen-

**TABLE 2** Solvent Effects on the Kinetic Parameters of Isomerization of Allyl Thiocyanate

| *Solvent* | *ET(30)* | *Δ G₃₅₈‡* (*kcal/mol*) | *Δ H‡* (*kcal/mol*) | *Δ S‡* (*cal k⁻¹ mol⁻¹*) | *Protic Solvent* |
|---|---|---|---|---|---|
| N-Methylformamide | 54.1 | 26.9 ± 0.3 | 19.0 ± 0.5 | −22.7 ± 0.8 | yes |
| 1-Propanol[a] | 50.7 | 26.7 ± 0.7* | 20.3 ± 1.5 | −17.7 ± 1.6 | yes |
| 2-Pyrrolidone | 48.3 | 27.0 ± 0.3 | 22.2 ± 0.6 | −13.7 ± 0.7 | yes |
| Dimethyl sulfoxide | 45.1 | 26.8 ± 0.3 | 18.0 ± 0.5 | −25.2 ± 0.8 | no |
| N,N-Dimethylformamide | 43.8 | 26.8 ± 0.4 | 20.5 ± 0.4 | −17.7 ± 0.9 | no |
| N,N-Dimethylacetamide | 43.7 | 26.7 ± 0.3 | 18.9 ± 0.5 | −22.7 ± 0.8 | no |
| N-Methyl-2-pyrrolidone | 42.2 | 26.2 ± 0.3 | 22.1 ± 0.6 | −13.7 ± 0.8 | no |
| Acetophenone | 40.6 | 26.7 ± 0.3 | 19.2 ± 0.5 | −21.5 ± 1.1 | no |
| Methyl isobutyl ketone | 39.4 | 26.9 ± 0.4 | 21.9 ± 0.4 | −14.1 ± 0.9 | no |
| Diisobutyl ketone | 38.0 | 26.8 ± 0.3 | 21.8 ± 0.5 | −14.6 ± 0.8 | no |
| Toluene | 33.9 | 26.7 ± 0.4 | 21.5 ± 0.3 | −14.9 ± 0.8 | no |

Initial concentration [$CH_2=CHCH_2SCN$] = 0.2 M.
[a]It was determined by $^1$H-NMR. *:359 K.

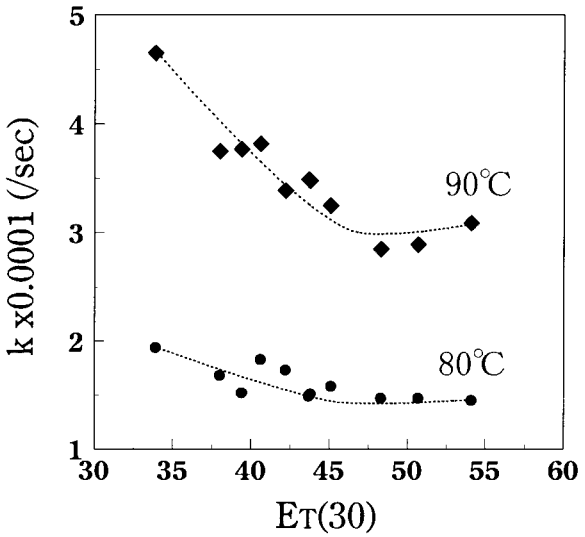


**FIGURE 1** Dependence of isomerization rate constant on solvent polarity.

**TABLE 3** Effects of Solvent on the Rate Constant ($\times 10^{-4}$ $s^{-1}$) of Isomerization

| *Solvents* | *Reaction* (*80°C*) | *Temp.* (*90°C*) |
|---|---|---|
| N-Methylformamide | 1.45 | 3.09 |
| 1-Propanol[a] | 1.47 | 2.89 |
| 2-Pyrrolidone | 1.47 | 2.85 |
| Dimethyl sulfoxide | 1.58 | 3.25 |
| N,N-Dimethylformamide | 1.51 | 3.48 |
| N,N-Dimethylacetamide | 1.49 | 3.49 |
| N-Methyl-2-pyrrolidone | 1.73 | 3.39 |
| Acetophenone | 1.83 | 3.82 |
| Methyl Isobutyl ketone | 1.52 | 3.77 |
| Diisobutyl ketone | 1.68 | 3.75 |
| Toluene | 1.94 | 4.65 |

Order of all rate constants are $\times 10^{-4}$ $s^{-1}$.
[a]86°C (359 K) and 92°C (365 K).

tal evidence that no thiocyanate was found after a sufficiently long period of heating, the isothiocyanate was found to be more stable than the thiocyanate by >3 kcal/mol in every calculation (see also Experimental).

It should be noted that, while the thiocyanate has a bent structure at the sulfur atom, the isothiocyanate has a linear structure at the C–N=C=S moiety. Since imines (C–N=C) [16], nitrites (O–N=O) [17], azo compounds (C–N=N=C) [17], carbodiimides (C–N=C=N–C) [18], and isocyanates (C–N=C=O) [18] are all known to show bent structures at nitrogen, the present finding with regard to the isothiocyanate is categorized as an exception.

*Potential Energy Surface Profile.* A potential energy surface profile of the transformation from the thiocyanate to the isothiocyanate is shown in Figure 3. Clearly depicted is the intrinsic reaction coordinate (IRC) that starts from the most stable conformation of the thiocyanate [allyl-SCN (RS)] and proceeds via a less stable conformation (C) in which the nitrogen atom of the thiocyano group approaches the carbon 1 atom, while the C3–S bond is lengthened, passing through the saddle point [*A* (TS)] to reach another stable structure [allyl-NCS (PS)], in which the C1–N bond is formed and the C3–S bond is completely broken. Finally, the isothiocyanate molecule assumes the most stable conformation. Although the four-membered cyclic TS, in which the C3–S breakage and the C1–N formation occurs at the same time, might be possible as an alternative for the six-membered ring TS [9], the four-membered ring structure is found to be of 80–90 kcal/mol higher

**TABLE 4** Total Energies Involved in the Isomerization between Allyl Thiocyanate and Allyl Isothiocyanate and Their Dependence on the Basis Sets

| *Basis Sets* | *Allyl-SCN* (*hartree*) | *Allyl-NCS* (*hartree*) | *TS* (*hartree*) | $\Delta E^b$ (*kcal/mol*) |
|---|---|---|---|---|
| RHF/3-21G* | −603.26049 | −603.30487 | −603.24029 | 12.7 |
| RHF/6-31G* | −606.30054 | −606.30846 | −606.24200 | 36.7 |
| RMP2/6-31G*[a] | −607.08111 | −607.08733 | −607.03590 | 28.4 |
| RMP3/6-31G*[a] | −607.11351 | −607.11617 | −607.05835 | 34.6 |
| RMP4/6-31G*[a](STDQ) | −607.16162 | −607.16747 | −607.11796 | 27.4 |

The RHF/6-31G* basis set was employed for calculating the structure.
1 Hartree = 627.5095 kcal/mol.
[a]On RHF/6-31G* optimized geometries.
[b]The values of process for allyl-SCN deformation to transition state.

**TABLE 5** Geometrical Parameters of the Most Stable Structures of (a) Allyl Thiocyanate and (b) Allyl Isothiocyanate

| | *Basis Sets* | | | |
|---|---|---|---|---|
| *Atoms* | *PM3* | *RHF/ 3-21G** | *RHF/ 6-31G** | *RHF/ 6-31G*** |
| (a) Allyl Thiocyanate | | | | |
| Bond lengths(Å) | | | | |
| C1–C2 | 1.329 | 1.135 | 1.138 | 1.317 |
| C2–C3 | 1.481 | 1.503 | 1.499 | 1.499 |
| C3–S | 1.829 | 1.842 | 1.841 | 1.840 |
| S–C4 | 1.657 | 1.692 | 1.706 | 1.706 |
| C4–N | 1.165 | 1.142 | 1.138 | 1.173 |
| C1–H1 | 1.098 | 1.073 | 1.077 | 1.077 |
| C1–H2 | 1.097 | 1.073 | 1.077 | 1.077 |
| C2–H3 | 1.086 | 1.074 | 1.075 | 1.077 |
| C3–H4 | 1.109 | 1.081 | 1.082 | 1.082 |
| C3–H5 | 1.109 | 1.082 | 1.082 | 1.082 |
| Bond angles (deg.) | | | | |
| C1–C2–C3 | 122.9 | 123.7 | 123.8 | 123.8 |
| N–C4–S | 176.9 | 178.9 | 179.3 | 179.3 |
| (b) Allyl Isothiocyanate | | | | |
| Bond lengths(Å) | | | | |
| C1–C2 | 1.328 | 1.314 | 1.317 | 1.316 |
| C2–C3 | 1.493 | 1.511 | 1.506 | 1.505 |
| C1–N | 1.450 | 1.442 | 1.431 | 1.431 |
| C4–N | 1.230 | 1.155 | 1.151 | 1.151 |
| C4–S | 1.499 | 1.606 | 1.609 | 1.609 |
| C3–H4 | 1.097 | 1.072 | 1.077 | 1.077 |
| C3–H5 | 1.097 | 1.073 | 1.077 | 1.077 |
| C2–H3 | 1.086 | 1.073 | 1.075 | 1.077 |
| C1–H1 | 1.109 | 1.083 | 1.084 | 1.084 |
| C1–H2 | 1.109 | 1.081 | 1.084 | 1.083 |
| Bond angles (deg.) | | | | |
| C1–C2–C3 | 122.3 | 123.2 | 123.5 | 123.4 |
| N–C4–S | 173.0 | 179.7 | 179.5 | 179.5 |

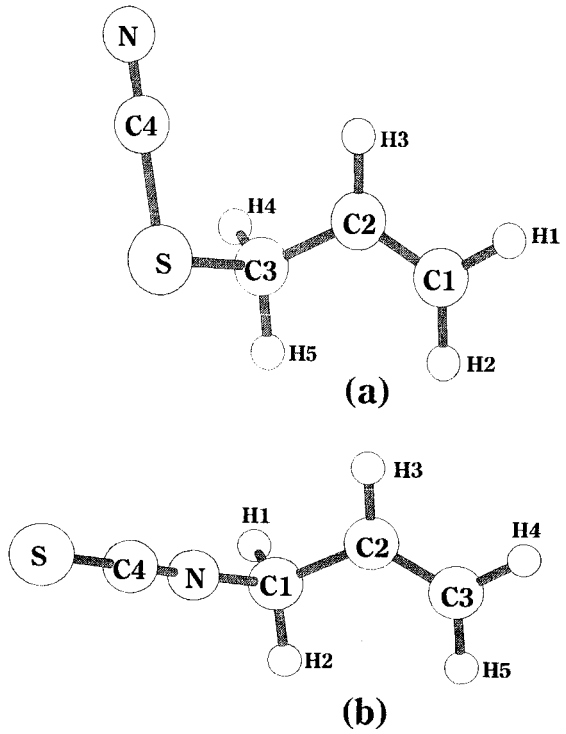


**FIGURE 2** Perspective views of the most stable structures of (a) allyl thiocyanate and (b) allyl isothiocyanate.

energy relative to the six-membered ring TS, being located at point *B* in the potential surface (Figure 3), and it is unlikely that the isomerization involves the four-membered ring TS. The optimized geometries of the six-membered cyclic TS are listed in Table 6, and the views of the structure are depicted in Figure 4. The allyl group is almost planar, and the thiocyanato group is slightly bent from the linear structure. The dihedral angles show that the thiocyanato group is almost astride the plane of the allyl group, as seen in Figure 4b. The distances are 2.75 and 2.20 Å, re-

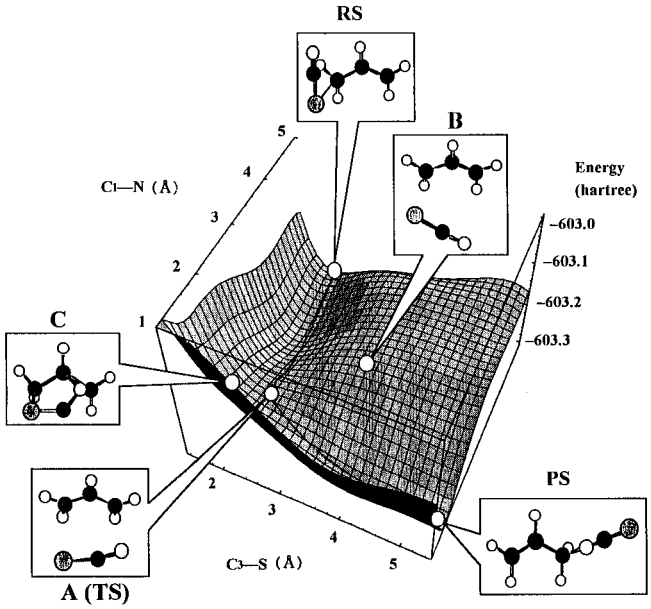


**FIGURE 3** Potential energy surface for the isomerization between allyl thiocyanate and allyl isothiocyanate.

spectively, for C–S and C–N. As it is clear from the side view (a) of the TS in Figure 4, the structure is far from the chair form, which is frequently seen in the TSs of Cope and Claisen rearrangements. Rather, the planes of the allyl group and the SCN group are almost perpendicular to each other, with the C–S distance a little larger than the C–N one.

It is also noted that even RHF/6-31G** gives a ca. 8 kcal/mol higher value than the experimental value ($\Delta H^{\neq}$). This indicates partly that we need further sophisticated basis sets for reproduction of the TS, as Houk admits that even the RHF/6-31G* basis set gives a ca. 10 kcal/mol higher activation energy than the observed [19] and partly that the solvent effect should be taken into consideration.

*Charge Distribution and Dipole Moments.* The dipole moment change of the complex was calculated as a function of the C1–N and C3–S distances and is shown schematically in Figure 5. Surprisingly, the charge separation in the TS is substantial, while in the RS (thiocyanate), it is very small, and in the PS, it is significant. The charge separation along the reaction path is shown in Figure 6. The charge separation at the TS amounts to 0.5–0.8e, depending on the basis sets used for calculation. This means that the cyclic TS formed in the reaction involves an ionic nature to a significant degree. We believe the methyl-substitution effects on the rates of allyl thiocyanate isomerization reported by Iliceto et al. [8] are due to this polarization.

**TABLE 6** Geometrical Parametes of the Transition State for the Isomerization

| | *Basis Sets* | | | |
|---|---|---|---|---|
| *Atoms* | *PM3* | *RHF/ 3-21G** | *RHF/ 6-31G** | *RHF/ 6-31G*** |
| Bond lengths (Å) | | | | |
| C1–C2 | 1.423 | 1.389 | 1.386 | 1.388 |
| C2–C3 | 1.406 | 1.366 | 1.365 | 1.365 |
| C3–S | 2.078 | 2.739 | 2.771 | 2.746 |
| C1–N | 1.691 | 2.194 | 2.226 | 2.199 |
| C4–S | 1.572 | 1.633 | 1.636 | 1.633 |
| C4–N | 1.217 | 1.160 | 1.160 | 1.160 |
| C1–H1 | 1.099 | 1.070 | 1.074 | 1.071 |
| C1–H2 | 1.102 | 1.071 | 1.073 | 1.071 |
| C2–H3 | 1.097 | 1.074 | 1.071 | 1.074 |
| C3–H4 | 1.095 | 1.073 | 1.072 | 1.072 |
| C3–H5 | 1.098 | 1.072 | 1.072 | 1.072 |
| Bond angles (deg.) | | | | |
| C1–C2–C3 | 121.5 | 119.8 | 119.7 | 119.8 |
| C1–C2–H3 | 118.5 | 119.1 | 119.9 | 119.2 |
| C1–N–C4 | 112.6 | 99.8 | 99.4 | 99.8 |
| C2–C1–N | 105.2 | 106.3 | 104.6 | 106.2 |
| C2–C1–H1 | 116.1 | 121.2 | 121.4 | 121.1 |
| C2–C1–H2 | 117.5 | 120.7 | 120.9 | 120.7 |
| C2–C3–S | 107.6 | 99.9 | 97.9 | 99.8 |
| C2–C3–H4 | 117.0 | 121.4 | 121.5 | 121.4 |
| C2–C3–H5 | 117.8 | 121.3 | 121.3 | 121.2 |
| C3–C2–H3 | 118.7 | 119.8 | 120.4 | 119.8 |
| C3–S–C4 | 90.1 | 82.5 | 82.5 | 82.4 |
| N–C1–H1 | 105.4 | 89.5 | 90.7 | 89.6 |
| N–C1–H2 | 99.7 | 87.6 | 86.2 | 87.5 |
| N–C4–S | 151.2 | 166.6 | 169.2 | 168.9 |
| S–C3–H4 | 102.3 | 94.9 | 97.0 | 94.9 |
| S–C3–H5 | 97.3 | 84.1 | 82.4 | 83.7 |
| Angle of torsion (deg.) | | | | |
| C1–C2–C3–S | 66.2 | 77.0 | 76.6 | 73.3 |
| C1–C2–C3–H4 | 180.6 | 175.4 | 179.8 | 75.4 |
| C1–N–C4–S | 4.8 | 5.3 | 5.5 | 5.2 |
| C2–C1–N–C4 | 27.4 | 31.3 | 32.0 | 31.4 |
| C2–C3–S–C4 | 27.8 | 28.3 | 28.7 | 28.2 |
| C3–C2–C1–N | 64.9 | 78.4 | 82.1 | 78.5 |
| C3–C2–C1–H1 | 179.0 | 178.1 | 178.0 | 178.1 |
| C3–S–C4–N | 4.4 | 4.0 | 4.1 | 3.9 |
| H3–C2–C1–N | 102.4 | 99.7 | 97.9 | 89.1 |
| H3–C2–C1–H1 | 13.8 | 10.8 | 2.0 | 10.5 |
| H3–C2–C1–H2 | 147.9 | 173.9 | 167.6 | 174.0 |
| H3–C2–C3–S | 101.0 | 77.0 | 103.4 | 94.2 |
| H3–C2–C3–H4 | 13.4 | 8.1 | 0.2 | 7.9 |
| H3–C2–C3–H5 | 150.5 | 177.0 | 170.7 | 177.1 |

*[3,3] Sigmatropic Reaction.* Since this reaction is now understood to be an example of a [3,3] sigmatropic shift, it may be worthwhile to compare the mechanism with those of other [3,3] sigmatropic shifts. Dewar et al. calculated the TSs of the Cope rearrangement and the Claisen rearrangement with use of the semiempirical AM1 method [20]. They

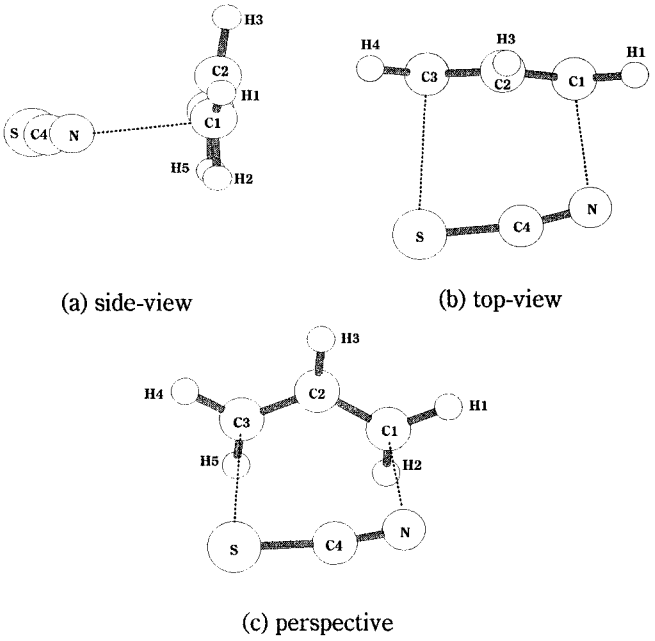


**FIGURE 4** Views of transition structure for the isomerization.

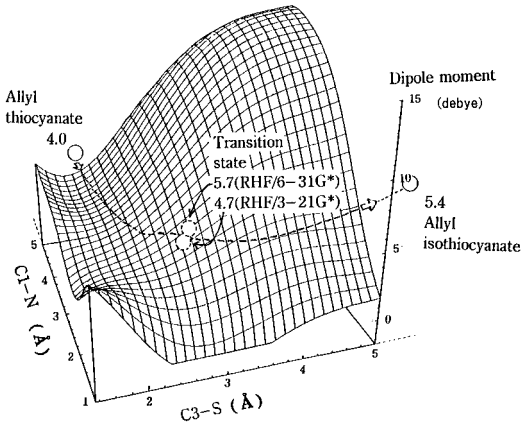


**FIGURE 5** Changes in dipole moments along the reaction path.

concluded that these were "concerted one step" reactions with the possibility of the TSs being biradicaloid. It was also noted that the TS of the Claisen rearrangement was more polar than the reactant, but the difference was small, whereas that of the Cope rearrangement was less polar than the reactant. Houk et al. recalculated the TS of the Claisen rearrangement by using RHF/6-31G* and CASSCF/6-31G*, and both H/D and heavy atom kinetic isotope effects were reproduced satisfactorily [21]. While, for the kinetic isotope effects, the sophisticated CASSCF/6-31G* level of calculation gives more satisfactory results than the RHF/6-31G* level, the

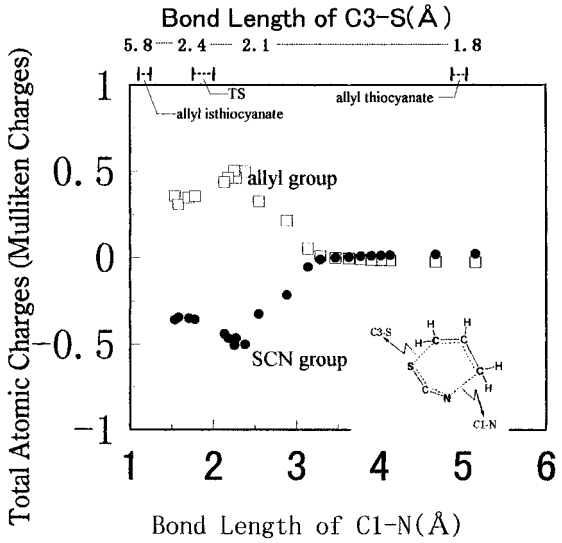


**FIGURE 6** Charge separation along the reaction path (RHF/3-21G* level).

latter will suffice for consideration of other factors that include a more favorable TS and geometry of the TS.

According to Houk et al., the TS of the Claisen rearrangement is close to the isolated vinyloxy and allyl moieties, with charge separation to some extent, the distance of C. . .C and C. . .O being 2.56 and 2.10 Å, respectively. The TS geometry of the present reaction is close to that of the Claisen rearrangement, but the separation of the two moieties, allyl and thiocyanate, is more distinct and the charge separation is more pronounced than in the Claisen case. Therefore, we can see that the rearrangement of allyl thiocyanate is categorized with [3,3] sigmatropic reactions of compounds that carry heteroatoms, such as the Claisen [21], azo-Cope [22], and oxy-Cope [23] rearrangements, its charge separation being distinct at the TS. However, there is one unique point in the TS structure of the thiocyanate isomerization. That is, while TSs are close to being in the chair form in other cases of [3,3] sigmatropic rearrangements, the present case shows a folded and distorted hexagon, because the S–C–N moiety is almost linear.

The charge-separated TS of the allyl thiocyanate isomerization raises a sharp question as to why the reaction rate is not influenced by the solvent polarity or is even slightly retarded in polar solvents. While the literature tells us that the Claisen rearrangement is accelerated by polar solvents [24], our results show that polar solvents somewhat retard the reaction under consideration here. It is also noted that there is a report [25] that the rearrangement of 2-(allylthio)-1,3-benzothiazole, which involves an S–C-

breaking and an N–C-making process, becomes faster in polar solvents than in nonpolar solvents [26]. Thus, solvent effects on the rates of rearrangement deserve further discussion.

*Electronic Structures and Solvent Effects.* The hypothesis of stronger solvation in the RS than in the TS is ruled out as a reason for the abnormal solvent effect, because we now know that the RS is less polar than the TS. We have to seek other reasons for the slightly retarded reactions in polar solvents.

In Table 2, our experimental results for the solvent effect are shown, where the solvents are divided into two categories, protic solvents and aprotic. Clearly protic solvents show some abnormal data when aprotic solvents are taken to be the norm. The features to be considered are that, in protic solvents, the rates of isomerization are invariant, whereas in aprotic polar solvents, there is retardation of the rate of the reaction. If solvents are aprotic, the presence of more polar solvents tend to promote a larger negative entropy of activation and a smaller enthalpy of activation than found in less polar solvents. It may be an example of enthalpy–entropy compensation [27], but it is worthwhile to discuss this phenomenon on the molecular basis as has been done in another case [28], because we have enough data available to do so.

We can tentatively attribute the observed tendencies as follows. The small enthalpy of activation found by use of polar solvents can be attributed to the stabilization of the polar TS by solvation. Thus, the enthalpy of activation becomes large as the solvent polarity decreases. At the same time, due to the strong solvation in the case of polar solvents, the degrees of freedom of motion of solvent molecules are more restricted at the TS than at the RS to make the entropy of activation more negative than that in the case of the presence of less polar solvents. A combination of these two factors causes the observed phenomena, i.e., slightly decreased rates of isomerization in polar solvents in comparison with those in less polar solvents. A protic solvent causes a definitely large enthalpy of activation and a smaller negative entropy of activation, as compared with the presence of an aprotic solvent of similar polarity. In a protic solvent, the stabilization by solvation is gained mainly by hydrogen bond formation. In the TS of isomerization, the positive and negative charges are delocalized considerably, and then it can be said that the TS of the substrate is soft in the sense of the hard-soft-acid-base (HSAB) theory [29]. Since a soft base is known to be less likely to form a hydrogen bond than a hard base, it will reduce the stability of the TS because of its poor solvation in the protic media, which makes the enthalpy of activation large. On the contrary, hydrogen bonds are extensively formed in the RS, and thus the less likelihood of hydrogen bond formation in the TS renders the entropy of activation positive as far as the influences of solvent molecules is concerned. Because entropy is decreased on going to the TS of the substrate from the RS due to the fact that the TS is cyclic, the sum of the entropy of activation of the system in protic media becomes less negative in comparison with the aprotic one. Of course, solvation of a polar nature cannot be overlooked even in the protic solvent case, and this gives the tendency that a more polar solvent in the protic series gives rise to a more negative entropy of activation than the less polar one. The net effect is that the factors enhancing and diminishing the reaction rates counterbalance each other.

## *EXPERIMENTAL SECTION*

*General Procedure of the Experiments.* The IR spectra were recorded on a Horiba FT-530 IR spectrometer as KBr discs. $^1$H NMR spectra were determined on a JEOL GSX-400 NMR spectrometer operating at 399.8 MHz. Dilute solutions in chloroform-*d* were used throughout with tetramethylsilane as the internal standard. Elemental analyses were performed by a PERKIN-ELMER 240C analyzer.

*Allyl Thiocyanate.* Bp 161°C. This compound was prepared as reported in the literature [30]. The sample gave satisfactory elemental analysis results and showed the following spectroscopic data ($CDCl_3$). $^1$H NMR: $\delta$ = 3.56 (2H, d, $J$ = 8.2 Hz), 5.35 (1H, d, $J$ = 7.6 Hz), 5.40 (1H, d, $J$ = 14.8 Hz), 5.88–6.00 (1H, m). IR: 2150 $cm^{-1}$ (C≡N, neat).

*Allyl Isothiocyanate* [31]. Bp 152°C. This compound showed the following spectroscopic data ($CDCl_3$). $^1$H NMR: $\delta$ = 4.15 (2H, dt, $J$ = 4.8 and 1.7 Hz), 5.29 (1H, d, $J$ = 10.2 Hz), 5.40 (1H, dd, $J$ = 17.0 and 1.6 Hz), 5.80–5.90 (1H, m). IR: 2080 $cm^{-1}$ (N=C=S, neat).

*Thermal Rearrangement.* A 0.20 M solution (20 mL) of allyl thiocyanate in an appropriate solvent was heated at 70–90°C with 5°C intervals. Thermo control was maintained by a TITEC oil bath shaker MH-10 (error ±0.1°C). An aliquot of 3.00 mL was taken from the sample solution with 10 minute intervals and chilled rapidly with ice water. The amount of the isothiocyanate was determined as described in the next section. At least five readings were obtained at a given temperature.

Rate constants were obtained similarly, with other concentrations as well as in the presence of additives, the representative values being shown in Table 3.

Although the presence of the isothiocyanate was not detected at an elevated temperature in solutions, it was detected by $^1$H NMR spectroscopy (ca. 5%) after long standing of the isothiocyanate in the neat state. The cause for this anomaly may be the difference in polarity of the environment. The stability of the thiocyanate, which is low relative to the isothiocyanate as an isolated molecule in the gas phase or in solutions of the present work, may be raised in the environment of the neat liquid.

*Product Analysis.* Determination of the isothiocyanate was carried out according to the method described in the literature [32]. To 3.00 mL of a solution of allyl isothiocyanate and allyl thiocyanate in dry toluene was added 3.00 mL of a ca. 0.2 M solution of dibutylamine in dry toluene, and the mixture was allowed to stand at room temperature for at least 1 hour to complete the reaction. 2-Propanol (50 mL) was added to the mixture, and the unreacted dibutylamine was titrated with 0.020 M hydrochloric acid, with use of bromophenol blue as an indicator. This method accounted for more than 99.0% of the existing isothiocyanate, except for the case of 1-propanol solvent, which accounted for 96.8%.

In some cases, the analysis was carried out with the use of $^1$H NMR spectroscopy. Both methods gave results in agreement with each other. The correlation coefficients were better than 0.990 for all the rate constants.

## *COMPUTATIONAL METHODS*

The Gaussian92 Program [33] was used throughout this study. The split-valence 6-31G* basis set was used for calculations of the transition state and the ground states of allyl thiocyanate and allyl isothiocyanate. The 3-21G* basis set was used for estimating the potential energy surface and atomic charges. The Møller-Plesset perturbation theory, MP2-4 methods, was applied for determination of theoretical activation energy. All calculations were performed on a Fujitsu 590tsp PC/AT machine, in which is installed a bug-fixed pentium processor.

The structures of the starting material and the product were first calculated by the PM3 method and optimized. An initial geometry set for optimization was prepared by rotating the allyl and SCN (or NCS) moieties around the C3–S (or C1–N) bond and selecting conformations at every 10° rotation for the starting material (or product). There were three energy minima by PM3 calculation for allyl thiocyanate. The geometries of the optimized structures were used for ab initio MO calculations at the RHF/6-31G* level, and an analytical frequency check was made. There exist numerous rotamers with respect to the C3–S single bond, which show energy differences of less than 3 kcal/mol from the most stable one of the thiocyanate. By contrast, the calculation for the isothiocyanate produced only one stable conformation about the (vinyl)C–C(isocyanato) bond. Only the most stable conformation of allyl thiocyanate is shown in Figure 2, with the structural parameters provided in Table 5. The TS was obtained by finding a structure with one negative frequency, as for usual optimization.

Potential surface was constructed by calculating structures for different distances of C–S and C–N with a 0.2 Å mesh. The surface is made by extrapolating with eighth-dimension functions. It is estimated that the surface may include ca. 6 kcal/mol error.

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