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## Origin of the Differential Acidity of Diastereotopic Protons in Sulfonium Salts

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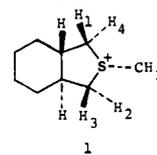
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**Abstract:** A semiquantitative model for prediction of the relative acidities of diastereotopic protons in sulfonium salts is presented. The model is based upon a reevaluation of the pertinent literature coupled with the insight provided by ab initio molecular orbital methods. In summary, the proton that lies most nearly perpendicular to the axis of the sulfur lone pair will undergo abstraction by base at the greatest rate. Minimization of line pair–lone pair repulsions in the intermediate ylide is postulated as the prime determinant of this behavior.

### Introduction

Carbanions stabilized by heteroatoms are widely known in organic chemistry and are well established as useful reagents in synthesis. The ylides of phosphorus<sup>2</sup> and sulfur<sup>2a,3</sup> have proved especially useful and have thus been the object of many experimental and theoretical investigations. In particular, the unique zwitterionic structure of these ylides has posed the theoretician with the difficult problem of devising a model for the bonding in such molecules, including a mechanism for stabilizing the negative charge at carbon.<sup>4</sup> One intriguing observation that has yet to be explained adequately is the difference in acidity of diastereotopic protons in the deprotonation reactions of trivalent sulfur compounds. The effect has been

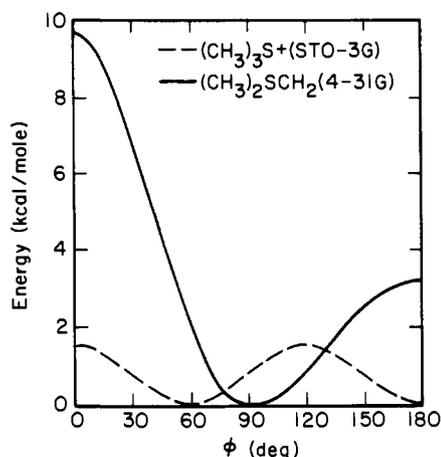
noted in the formation of sulfinyl carbanions<sup>5</sup> as well as in the ylide-forming reaction of sulfonium salts.<sup>6</sup> Fava and co-workers have measured the rate of deuterium incorporation into a variety of sulfonium salts under conditions of base catalysis. One such system studied is the thioniabicyclo[4.3.0]nonane **1**.<sup>6c,f</sup> The four unique protons in **1** undergo exchange with relative rates of H<sub>1</sub>:H<sub>2</sub>:H<sub>3</sub>:H<sub>4</sub> = 1:90:700:90.



**Table I.** Rate Data for Exchange of Protons in Sulfonium Salts (75 °C)

compd	$\phi^a$	$K_2(75\text{ }^\circ\text{C})^b$	$k_{\text{rel}}^c$	$\Delta E_a,^d$ kcal	$\Delta G_{4-31G}^e$	ref
3	5, 25 <sup>f</sup>	$5.7 \times 10^{-6}$	$7.0 \times 10^{-3}$	3.4	7.7 <sup>g</sup>	6b,c
3	105, 120 <sup>f</sup>	$1.7 \times 10^{-4}$	$2.1 \times 10^{-1}$	4.1	0.2 <sup>h</sup>	6b,c
4	55	$1.6 \times 10^{-5}$	$2.0 \times 10^{-2}$	2.7	2.7	6b,g
4	175	$4.4 \times 10^{-7}$	$2.2 \times 10^{-3}$	5.2	3.2	6b,g
5	90 <sup>i</sup>	$8.2 \times 10^{-4}$	1.0	0	0	6f
1	5	$10^{-7}$	$1.2 \times 10^{-4}$	6.2	9.6	6f
1	30	$7.1 \times 10^{-6}$	$8.7 \times 10^{-3}$	3.3	7.0	6f
1	105	$5.0 \times 10^{-4}$	$6.1 \times 10^{-1}$	0.3	0.2	6f
1	135	$7.1 \times 10^{-6}$	$8.7 \times 10^{-3}$	3.3	1.7	6f

<sup>a</sup> From Dreiding models. <sup>b</sup> Per proton. <sup>c</sup> Exchange rate with respect to the exocyclic methylene in **5**. <sup>d</sup> Estimated from  $k_{\text{rel}}$ :  $\Delta E_a = -RT(\ln k_{\text{rel}})$ . <sup>e</sup> From Figure 1. <sup>f</sup> These protons are rendered equivalent by conformational processes. <sup>g</sup> Assuming  $\phi = 25^\circ$ . <sup>h</sup> Assuming  $\phi = 105^\circ$ . <sup>i</sup> Here  $\phi$  is taken to be the minimum point on the energy surface since all conformations are accessible to the exocyclic methylene proton in **5**.

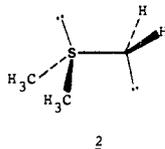


**Figure 1.** Calculated energy function for rotation about the ylide C-S bond in dimethylsulfonium methylene (4-31G) and the C-S bond in trimethylsulfonium ion (STO-3G).

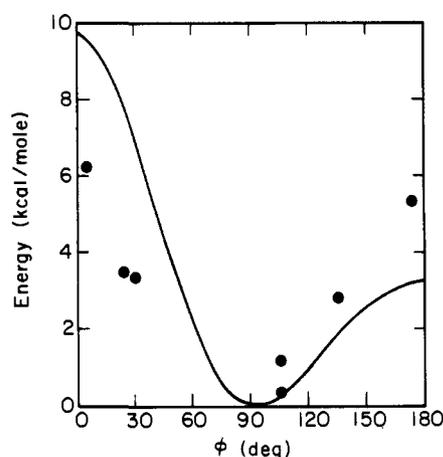
These interesting results led us to investigate sulfonium salts as possible intermediates en route to complex macrocyclic natural products.<sup>7</sup> Our progress was hampered by the lack of a reliable method for the prediction of the relative acidities of diastereotopic protons in these systems. The current study was undertaken to remedy that situation. We find that, contrary to recent assertions,<sup>6f</sup> there is a simple relationship between the acidity of a given proton and the dihedral angle between C-H bond axis and the sulfur lone pair. This proposition is based upon a critical review of the experimental data relating to this differential acidity effect coupled with the insight provided by ab initio molecular orbital calculations.

### Methods and Results

Standard restricted Hartree-Fock theory (the GAUSSIAN 70 series of programs)<sup>8a</sup> with a small split valence basis set (4-31G)<sup>8b</sup> was used to calculate a cross section of the potential surface for rotation in the simplest ylide, dimethylsulfonium methylene (**2**). The ylide carbon was assumed to be pyramidal.



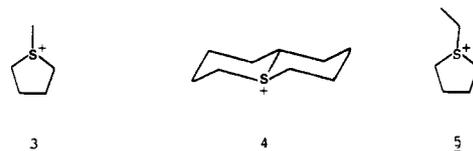
Bond lengths and angles at sulfur were assigned average values derived from X-ray crystallographic<sup>7b,9</sup> studies:  $\angle\text{CSC} = 105^\circ$ ,  $r_{\text{C-S}} = 1.85 \text{ \AA}$ . Pople's standard carbon-hydrogen bond lengths and H-C-S bond angles were used.<sup>8c</sup> The two S-methyl groups were held in fixed, staggered conformations. Rigid rotation



**Figure 2.** Comparison of the theoretical rotational potential for dimethylsulfonium methylene and experimental energies of activation for deprotonation of rigid sulfonium ions.

about the C-S (ylide) bond in  $30^\circ$  increments and calculation of the energy of the system at each point generated the curve depicted in Figure 1. The dihedral angle  $\phi$  is defined to be zero when the adjacent lone pairs are eclipsed. The calculated energy of the minimum-energy conformation,  $\phi = 90^\circ$ , is  $-514.98642 \text{ au}$ . The STO-3G energy profile for rotation in the parent salt,  $(\text{CH}_3)_3\text{S}^+$ , is reproduced in Figure 1 for comparison.

We hoped that there would be a correlation between the calculated relative gas phase stability of a given ylide conformation and the observed exchange rates in water solution. Thus the rate data available for several sulfonium salts (**1**, **3**, and **4**)



were extrapolated to a single temperature (75 °C) and tabulated as a function of dihedral angle (Table I). The dihedral angles were measured from Dreiding models<sup>10</sup> using the standard set of bond lengths and angles. In addition the relative rate of exchange of each proton is reported with respect to the exocyclic methylene protons in **5**, as well as the estimated difference in activation energy,  $\Delta E_a$ .<sup>11</sup>

Figure 2 presents a plot of the  $\Delta E_a$  values obtained superimposed on Figure 1. The agreement is rather remarkable. The deviation from the theoretical curve may be readily attributed to the effects of solvation encountered upon translation of the ylide from the gas phase (our calculation) to water solution (vide infra).

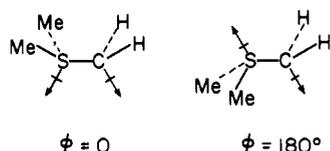


Figure 3. Illustrating the interaction of lone pair dipoles in the  $\phi = 0^\circ$  and  $\phi = 180^\circ$  conformations of dimethylsulfonium methylide.

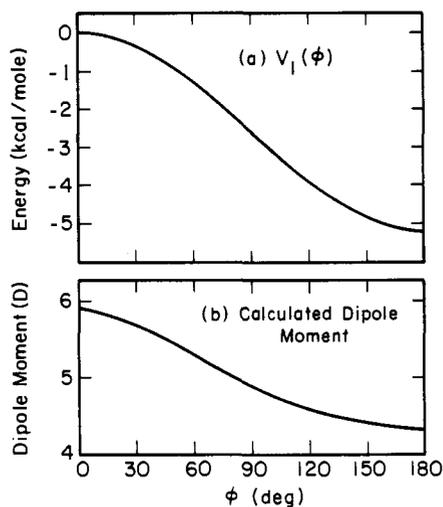


Figure 4. (a) The  $V_1(\phi)$  term obtained by Fourier decomposition of  $V(\phi)$  for rotation about the ylide C-S bond of dimethylsulfonium methylide. (b) Theoretical dipole moment of dimethylsulfonium methylide as a function of rotation about the ylide C-S bond.

## Discussion

An interpretation of the shape of the potential curve (Figure 1), and thus the origin of the differential acidity effect, is facilitated by the technique of Fourier decomposition. Pople<sup>12</sup> has previously used this approach to dissect the potential function for internal rotation in a variety of molecules into several component functions that may be simply interpreted in terms of some physical property of the molecule. The three-term series  $V(\phi) = \frac{1}{2}V_1(1 - \cos \phi) + \frac{1}{2}V_2(1 - \cos 2\phi) + \frac{1}{2}V_3(1 - \cos 3\phi)$  reproduces Figure 1 almost exactly when  $V_1 = -5.2$ ,  $V_2 = -6.7$ , and  $V_3 = -1.3$  kcal/mol.

The  $V_3$  term can be readily attributed to torsional interactions. The negative sign indicates that staggered conformations are preferred to eclipsed geometries. In fact,  $V_3$  is of the same magnitude as the threefold symmetric rotational barrier in the parent salt.

The  $V_1$  term has been attributed to a local dipole moment interaction in several systems.<sup>12</sup> The same interpretation is favored here. The dipoles associated with the adjacent lone pairs destabilize the  $0^\circ$  conformation of the ylide, with respect to the  $180^\circ$  conformation (Figure 3). The dipole moment calculated for **2** at the 4-31G level is plotted as a function of rotation (Figure 4a). Comparison of this function to  $V_1(\phi)$  (Figure 4b) seems to confirm the hypothesis.

The twofold term,  $V_2(\phi)$ , is the largest term among the contributors to the rotational potential. We have noted that  $V_2(\phi)$  is essentially identical in magnitude and shape with the variation in the energy of the highest occupied molecular orbital ( $E_{\text{HOMO}}$ ) with rotation (Figure 5). Thus it seems that some variation in the stabilization of the HOMO is responsible in large part for the  $V_2$  term. Examination of the coefficients of the atom-centered orbitals contributing to the HOMO reveals that this orbital essentially describes the carbon lone pair.

There are two other contributions to this orbital which are well illustrated by a Jorgensen<sup>13</sup> plot of the HOMO in each

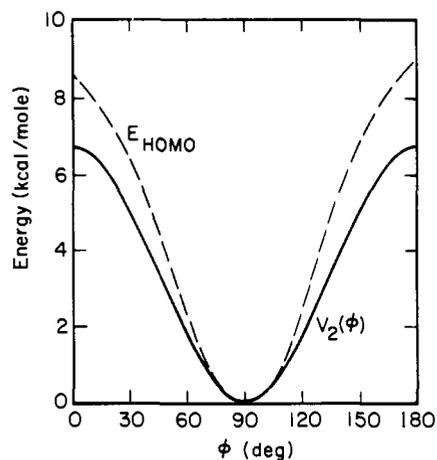


Figure 5. The  $V_2(\phi)$  term obtained by Fourier decomposition of  $V(\phi)$  for rotation about the ylide C-S bond in dimethylsulfonium methylide (solid line) compared with the computed energy of the highest occupied molecular orbital (dashed line).

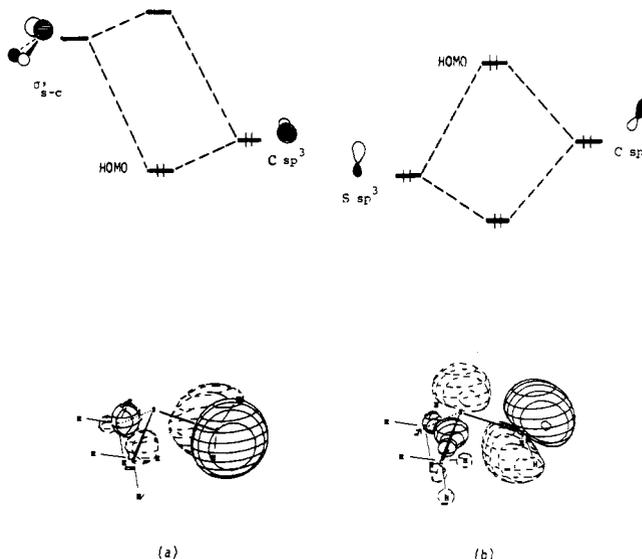


Figure 6. Jorgensen plot and simple perturbation theory derivation of the highest occupied molecular orbital of dimethylsulfonium methylide in two selected conformations: (a)  $\phi = 90^\circ$ ; (b)  $\phi = 0^\circ$ .

of two conformations. The first interaction can be envisioned to arise from mixing the lone pair on carbon with an orbital that is  $\sigma$  antibonding between sulfur and the methyl group. This interaction between one filled (lone pair) and one vacant (C-S  $\sigma^*$ ) orbital provides a stabilization energy (Figure 6a). The significance of this interaction has been discussed by several workers,<sup>4d,6g,14</sup> and has been termed "anionic hyperconjugation". The second interaction is that between adjacent lone pairs (Figure 6b). This four-electron interaction involving two orbitals is net destabilizing. We now provide evidence that the conformational preferences in sulfonium ylides are due to the second effect.

Fava, Bernardi, and co-workers<sup>6g</sup> have used the results of the Mulliken overlap population analysis to advance the idea that the hyperconjugative interaction discussed above is conformationally dependent. A series of three compounds, methylthanium cation **6** and the two diastereomeric ylides **7** and **8**, were studied. The experimentally observed preference for proton abstraction leading to the ylide **7**, in rigid sulfonium salts related to **6**, was correlated with the observation that the total overlap population of the bond antiperiplanar to the lone

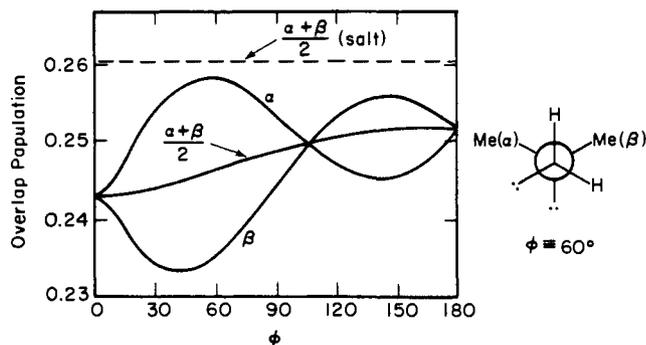


Figure 7. Mulliken population analysis of dimethylsulfonium methylide as a function of rotation about the ylide C-S bond; overlap populations of the S-CH<sub>3</sub> bond.

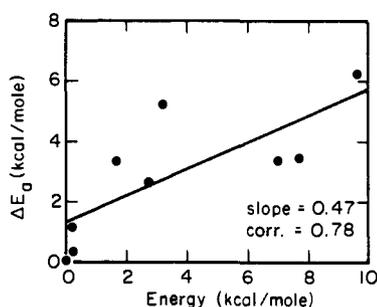


Figure 8. Brønsted plot of the data presented in Figure 2.

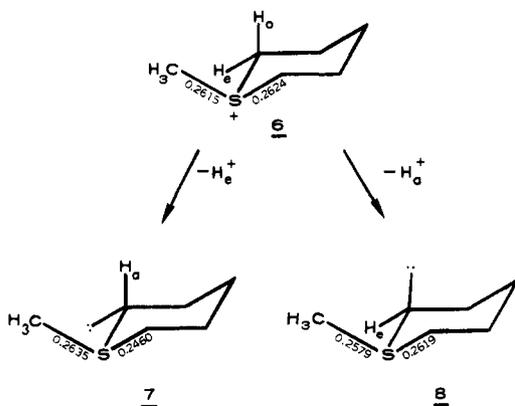


Figure 9. Comparison of the experimental energies of activation for deprotonation of rigid sulfonium ions with the quantity  $V(\phi) = \frac{1}{2}V_2(1 - \cos 2\phi) + \frac{1}{2}V_3(1 - \cos 3\phi)$  for rotation about the ylide C-S bond in dimethylsulfonium sulfide.

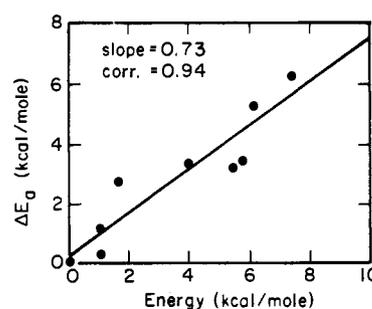


Figure 10. Brønsted plot for the data presented in Figure 9.

pair in **7** decreased more upon deprotonation than either of the bonds in the alternative ylide **8** (compared to the salt **6**).

Of course the caveats associated with the Mulliken population analysis are well known,<sup>15</sup> but, even assuming that the method is reliable, we find a more serious problem in the interpretation of these results. Since there are two adjacent acceptor orbitals in the ylide, one should consider the linear combination of both these orbitals as they interact with the lone pair on carbon. This is intuitively reasonable. As the carbon lone pair rotates away from coplanarity with a given bond, favorable overlap is certainly sacrificed. This will be at least partly compensated by an increased overlap with the other bond. Thus we expect that the total overlap population in each bond will vary sinusoidally but since the two curves are out of phase the net effect is to provide nearly constant delocalization of the carbon lone pair with rotation. Our calculations<sup>16</sup> confirm this point (Figure 7). While large fluctuations in the individual bond populations are noted, the average population is almost invariant with conformation. It may be significant that the overlap population in these bonds is less in the ylide than in the salt. However, even if this "hyperconjugation" mechanism is partially responsible for net stabilization of the ylide, it does not account for its conformation and therefore

does not account for the differential acidity of diastereotopic protons in sulfonium salts. This leaves lone pair-lone pair interaction as the only clear alternative to explain the  $V_2$  term. This repulsive interaction will be minimized in the 90° conformation where these orbitals are orthogonal, and the ylide therefore prefers this geometry.

We return now to the question of the differences between the experimentally determined rates of proton-deuteron exchange and our 4-31G potential surface. The first effect is a compression of the energy scale for  $\Delta E_a$ ; that is, for a given pair of protons the 4-31G potential tends to overestimate the difference in exchange rates. Kinetic and equilibrium acidities are usually related by the Brønsted equation:<sup>17</sup>

$$\log k = \alpha \log K + C \quad (\alpha \leq 1)$$

A Brønsted-type plot of  $\Delta E_a$  vs. the energy calculated for the corresponding conformation of ylide **2** shows that this general trend is seen here (Figure 8). The least-squares line gives a value for  $\alpha$  of 0.45 (corr = 0.78).

If our interpretation of the nature of the rotational barrier in the ylide system is correct, we can make intuitive corrections to the shape of the curve that will account for solvation. The largest effect should be the attenuation of the dipole-moment term,  $V_1$ . Figure 9 depicts the experimental data superimposed on a plot of  $V(\phi) = \frac{1}{2}V_2(1 - \cos 2\phi) + \frac{1}{2}V_3(1 - \cos 3\phi)$ . The agreement is clearly improved as is illustrated by the improvement in the Brønsted correlation (Figure 10,  $\alpha = 0.73$ , corr = 0.94). We propose that the semiempirically derived curve in Figure 9 represents a useful tool for predicting the relative acidities of diastereotopic protons in rigid sulfonium salts.<sup>18</sup>

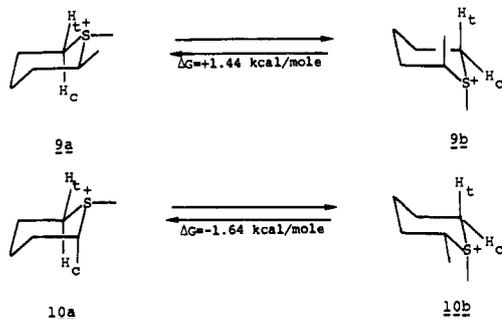
The case of conformationally mobile sulfonium salts is more difficult to deal with, but from Fava's work<sup>6g</sup> it is clear that loss of rigidity generally results in loss of stereoselectivity in exchange reactions. For instance, *S*-methylthianium salt **3** shows

Table II

compd	proton	$\phi$	conf energy	+	$E_a$	=	activation barrier
9a	H <sub>t</sub>	50	0	+	25	=	25.0 kcal/mol
9a	H <sub>c</sub>	165	0	+	27.2	=	27.2 kcal/mol
9b	H <sub>t</sub>	55	1.4	+	24.7	=	26.1 kcal/mol
9b	H <sub>c</sub>	65	1.4	+	23.6	=	25.0 kcal/mol

essentially no stereoselectivity in exchange reactions.<sup>6b,d</sup> This can be attributed to small conformational deformations that distort the molecule in such a way that two seemingly different ylides can achieve energetically equivalent structures.

An alternative is interconversion of proton environments by a process such as chair-chair flip in **3**. The latter requires that the barrier separating the two conformers be considerably less than the activation barrier for the proton-exchange reaction. This latter possibility would certainly seem to be the case for **3**, where the two conformers are probably separated by a barrier of no more than 10 kcal/mol (the barrier for chair-chair interconversion in cyclohexane) and the activation energy for the exchange reaction is on the order of 25 kcal/mol.<sup>6b</sup> Eliel has argued<sup>19</sup> that rapid chair-chair interconversion is not responsible for the fact that the two C-6 protons in each of the *S*,2-dimethylthanium salts **9** and **10** undergo exchange at



essentially the same rate.<sup>20</sup> The observed conformational equilibria of **9** and **10** were cited as evidence for this theory. Since conformer **10a**, for example, comprises greater than 90% of the equilibrium mixture of **10** under the conditions of the exchange reaction, Eliel concluded that site interconversion is *not* the mechanism by which nonselectivity is obtained. Such a conclusion may not be warranted by this evidence since it conflicts with the Curtin-Hammett principle.<sup>21</sup>

The activation barriers for exchange of each type of proton in **9** may be estimated from our Figure 9, the Brønsted relationship, and Dreiding models.<sup>22</sup> We have chosen an activation barrier of 25 kcal/mol for exchange of H<sub>t</sub> in **9a** as a reference point. The remaining data are summarized in Table II. The data is displayed in the form of a reaction-coordinate diagram (Figure 11). What is interesting is that there are pathways of comparable energy for the exchange of either H<sub>c</sub> or H<sub>t</sub>, the former proceeding via the intermediacy of the less populated conformer of **9**. We do not claim arithmetical rigor in this approach. We do wish to emphasize the fact that upon conformational interconversion the activation barrier for the exchange of a given proton may be affected more than the ground-state energy is affected by the conformational process.

## Conclusions

We have presented a model for the deprotonation reactions of sulfonium salts. We find that a relatively simple function correlates the dihedral angle between the sulfur lone pair and the C-H bond axis with the acidity of a given proton. Thus we have accomplished our primary goal in the present study, providing a predictive tool for the deprotonation behavior of

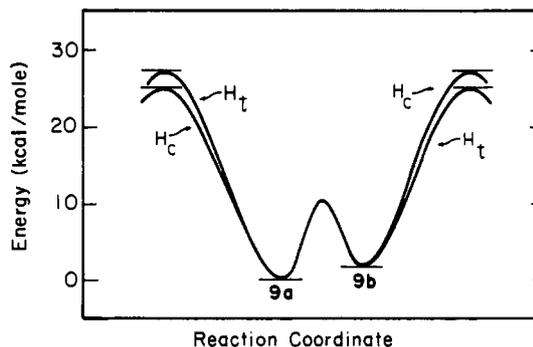


Figure 11. Reaction coordinate diagram for deprotonation of *S*-methylthanium ions. H<sub>c</sub> and H<sub>t</sub> are the protons cis and trans to the methyl group.

sulfonium salts. We cannot at this point provide definitive information regarding the structure of the sulfonium ylide. Our assumption that carbon is pyramidal in such species is clearly supported by the agreement obtained between experiment and calculation. We note that the question of d-orbital participation has not been addressed here, although the agreement between our calculated results and experiment suggests that these play no role in determining conformational preferences in the ylide system.

We are currently involved in carrying out more sophisticated calculations on the ylide system in an effort to draw definitive conclusions regarding the bonding and structure in these molecules. In addition, our experimental work continues in this field in an effort to corroborate our theoretical model.

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- (17) See ref 3b, p 36, and references cited therein.
- (18) An alternative explanation for the diminution of the  $V_1$  term is that at the transition state for deprotonation the carbon is planar. In such a case  $V_1$  must be zero owing to the symmetry of the system. Other experimental data<sup>7b</sup> indicates this not to be the case.
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## Transition State Vibrational Analysis for the Methyl Isocyanide Rearrangement, $\text{CH}_3\text{NC} \rightarrow \text{CH}_3\text{CN}$

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**Abstract:** The title reaction is perhaps the most exhaustively studied of all unimolecular reactions to be examined by the experimental methods of modern chemical kinetics. Previous theoretical work on this and the related  $\text{HNC} \rightarrow \text{HCN}$  reaction appears to demonstrate that the  $\text{CH}_3\text{NC} \rightarrow \text{CH}_3\text{CN}$  potential energy surface is qualitatively described within the Hartree-Fock approximation. In the present ab initio self-consistent-field study, a double  $\zeta$  plus polarization basis set, described as C(9s 5p 1d/4s 2p 1d), H(4s 1p/2s 1p), N(9s 5p 1d/4s 2p 1d), was employed. The transition state or saddle point for the  $\text{CH}_3\text{NC}$  rearrangement was precisely located using gradient techniques. The same methods were used to evaluate the harmonic vibrational frequencies about the transition state or activated complex. Although the transition-state structure is quite different from that suggested by Schneider and Rabinovitch, the present theoretical vibrational frequencies are in surprisingly good agreement with those deduced from experiment via the RRKM hypothesis. Using the ab initio rotational and vibrational parameters in conjunction with activated-complex theory yields experimental rate constants about 50% greater than experiment.

### Introduction

The Rice-Ramsperger-Kassel-Marcus (RRKM) theory is one of the pillars of modern chemical kinetics.<sup>1,2</sup> The chief merits of RRKM, of course, are its simplicity and typical order-of-magnitude correctness. Furthermore, over the years the method has proven quite adaptable to the incorporation of quantum effects and other refinements.<sup>3</sup> The most obvious criticism of RRKM theory as it is widely used is that it contains a number of empirically adjustable parameters, namely, the transition state vibrational frequencies and moments of inertia. These are sometimes empirically deduced from the experimental rate constants. Since transition state vibrational frequencies cannot be measured experimentally, it has been somewhat difficult to assess the absolute validity of RRKM.

Probably the most exhaustive examination of the RRKM theory has been carried out by Rabinovitch and co-workers<sup>4-7</sup> for the methyl isocyanide isomerization



In this respect the correspondence between Bunker and Rabinovitch<sup>8-11</sup> concerning whether or not  $\text{CH}_3\text{NC}$  is an "RRKM molecule" is of special interest. Schneider and Rabinovitch<sup>4</sup> have assigned transition state vibrational frequencies for (1), but they conclude that the twisting vibration is a significant and arbitrary frequency. Moreover, different values for the other frequencies are clearly possible. If reliable values of all frequencies could be determined theoretically, an im-

mediate assessment of the RRKM method would be possible.

Several other experimental studies of the  $\text{CH}_3\text{NC}$  isomerization have also been reported, including thermal,<sup>12</sup> photochemical,<sup>13</sup> hot atom chemistry,<sup>14</sup> and most recently laser spectroscopic studies.<sup>15-17</sup> For example, in their recent laser study Reddy and Berry<sup>15</sup> were able to photoisomerize  $\text{CH}_3\text{NC}$  by directly pumping the fourth overtone of the CH stretch. Even more recently Guillory and co-workers<sup>17</sup> observed (among products other than  $\text{CH}_3\text{CN}$ ) CN, CH, and  $\text{C}_2$  from their infrared multiphoton photolysis of  $\text{CH}_3\text{NC}$ . However, they concluded that the isomerization of  $\text{CH}_3\text{NC}$  occurs quantitatively at energies just above threshold, and other products result from the secondary photolysis of  $\text{CH}_3\text{CN}$ . With this number and variety of experimental studies, it is no wonder that the methyl isocyanide rearrangement has been the target of several theoretical investigations.

### Theoretical Background and Present Approach

At least five distinct theoretical studies of the methyl isocyanide rearrangement have been reported, ranging from extended Hückel<sup>18</sup> to MINDO<sup>19</sup> to ab initio studies.<sup>20-22</sup> Interestingly, none of the ab initio studies has precisely determined the transition-state geometry in the manner possible using modern gradient techniques.<sup>23</sup> However, the self-consistent-field (SCF) transition state of Liskow, Bender, and Schaefer (LBS),<sup>20</sup> obtained from a double  $\zeta$  (DZ) basis set, should be quite close to the true DZ SCF saddle point. An in-