Photodissociation of Nitrosobenzene and Decomposition of Phenyl Radical†

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Received: February 9, 2004; In Final Form: March 23, 2004

Photodissociation of nitrosobenzene in a molecular beam has been studied by multimass ion imaging techniques. Photodissociation at 248 nm shows that there is only one dissociation channel, i.e., C₆H₅NO → C₆H₅ + NO, regardless of the fact that the other channel, C₆H₅NO → C₆H₅ + HNO, is energetically accessible in agreement with theoretically predicted results. Photodissociation at 193 nm also shows the same dissociation channel. However, about 10% of the C₆H₅ radicals produced at this wavelength further decomposed into benzene and H atom, and the dissociation rates of phenyl radical as a function of internal energies were measured. The averaged photofragment translational energies released from the dissociation of nitrosobenzene at 193 and 248 nm are 10.2 and 6.9 kcal/mol, respectively, and fragment distributions are almost isotropic at both wavelengths. In addition, the thermal rate constant for dissociation of C₆H₅NO has been computed and compared with experimental data; the agreement between theory and experiment is excellent, confirming the most recently reported unusually high A-factor (>10¹⁷ s⁻¹).

I. Introduction

Nitrosobenzene has been popularly employed photolytically as the precursor of phenyl radicals in many kinetic and spectroscopic studies because of its large extinction coefficient in the UV region.¹–⁸ The molecule has a large energy gap between the S₁ and S₂ states.⁹,¹⁰ Hence, the possibility of fluorescence from the S₂ state has been discussed.¹¹ However, no fluorescence has been observed.¹²–¹⁴ The existence of a fast decay channel in the S₂ state is therefore expected. Indeed, it was found that the dissociation of nitrosobenzene in argon matrices at 12 K is very efficient upon irradiation of UV photons.¹⁵

The dynamics of photodissociation of nitrosobenzene in the gas phase have been studied recently.¹⁶–²² However, conclusions are very different from these studies. Dick and co-workers²² measured the absorption spectrum of the S₀ → S₂ transition of the ultracold nitrosobenzene in a supersonic jet. A lifetime of the S₂ state determined directly by the homogeneous line width of the absorption spectrum was found to be 60 ± 3 fs. They also measured the alignment, velocity distribution, and populations of the rotational and vibrational states of the NO fragments via laser-induced fluorescence and ion imaging technique at various UV wavelengths.¹⁸–²⁰ Fragments have an isotropic velocity distribution and no alignment was observed. In addition, the NO rotational population has a statistical distribution and only 10% of the NO fragments are produced in vibrational excited states. They concluded that the primarily populated Sₙ state (n ≥ 2) decays rapidly through internal conversion to the S₁ or S₀ state, and the dissociation occurs through a statistical mechanism on the potential surface of the lower state on a time scale much slower than rotation of the parent molecule. On the other hand, Han and co-workers²¹,²² also have studied the photodissociation of nitrosobenzene at 266 nm recently. The anisotropy parameter β = −0.64 was found from the time-of-flight spectra of NO and C₆H₅ photofragments. Their laser-induced fluorescence study also demonstrated that more than 60% of the NO fragments are populated in the vibrational excited state and the NO fragment rotational temperature is much higher than that measured by Dick et al.

In all existing studies, including those kinetic and spectroscopic papers cited above, only one dissociation channel, C₆H₅NO → C₆H₅ + NO, has been assumed and/or detected in the photodissociation of nitrosobenzene in the UV region, despite the fact that the C₆H₅ + HNO product channel is accessible at 248 nm while the C₆H₅ + H + NO product channel becomes energetically accessible at 193 nm.

In this report, photodissociation of nitrosobenzene at 193 and 248 nm was studied by multimass ion imaging techniques. Particular attention has been focused on the search for the other possible dissociation channel and the fragment anisotropy measurement. In addition, the decomposition of the phenyl radical produced from the photodissociation reaction and the thermal decomposition of nitrosobenzene were also studied; the data will be discussed in reference to the ab initio MO and statistical theory results.

II. Experimental Section

Experimental Setup. The experimental techniques have been described in detail in our previous reports on other aromatic molecules,²³–²⁶ and only a brief description is given here.

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study the unimolecular reaction of C\textsubscript{6} H\textsubscript{5} NO based on our earlier states, as well as by the normal-mode analysis. To continue trajectories of Figure 1.

The nitrosobenzene vapor was formed by flowing ultrapure He at pressures of 500 Torr through a reservoir filled with sample at 293 K. The nitrosobenzene/He mixture was then expanded through a 500 \( \mu \text{m} \) pulsed nozzle to form the molecular beam. Molecules in the molecular beam were photodissociated by an UV laser pulse. Due to the recoil velocity and center-of-mass velocity, the fragments were expanded to a larger sphere on their flight to the ionization region and then ionized by a VUV laser pulse. The distance and time delay between the VUV laser pulse and the UV photolysis laser pulse were set such that the VUV laser beam passed through the center-of-mass of the dissociation products and generated a line segment of photofragment ions by photoionization. The length of the segment was proportional to the fragment recoil velocity in the center-of-mass frame multiplied by the delay time between the photolysis and the ionization laser pulses. To separate the different masses within the ion segment, a pulsed electric field was used to extract the ions into a mass spectrometer after ionization. While the mass analysis was being executed in the mass spectrometer, the length of each fragment ion segment continued to expand in the original direction according to its recoil velocity. At the exit port of the mass spectrometer, a two-dimensional ion detector was used to detect the ion positions and intensity distribution. In this two-dimensional detector, one direction was the recoil velocity axis and the other was the mass axis. The schematic diagram of the experimental setup is shown in Figure 1.

Computational Method. The hybrid density functional B3LYP\textsuperscript{27–29} with three split valence basis sets, 6-31G(d), 6-31+G(d), and 6-31G(2df,p), has been applied to optimize the geometries of the reactant, intermediate, transition state, and products with tight convergence criteria. All the stationary points were identified by the number of imaginary frequencies (NIMG) with NIMG = 0 for stable species and NIMG = 1 for transition states, as well as by the normal-mode analysis. To continue to study the unimolecular reaction of C\textsubscript{6}H\textsubscript{5}NO based on our earlier work\textsuperscript{28} at the G2M(rcc, MP2) and G2M(RCC, MP2) levels\textsuperscript{31} in this report we also performed quantum-chemical calculations with the G2M(RCC, MP2) scheme. A series of single-point energy calculations for the G2M(RCC, MP2) composite scheme using the geometries and zero-point energy (ZPE) corrections from the B3LYP/6-31G(d) and B3LYP/6-31+G(d) levels of theory have been carried out to obtain more reliable information on energetics for the potential energy surface (PES) and the rate constant prediction by

\[
E_0 \text{[G2M]} = \text{RCCSD(T)/6-311G(d,p)} + \text{MP2/6-311+G(3df,2p)} - \text{MP2/6-311G(d,p)} + \Delta \text{HLC + ZPE}
\]

The empirical \( \Delta \text{HLC} \) is given by \(-5.3n_\beta - 0.19n_\alpha \) in millihartrees, where \( n_\alpha \) and \( n_\beta \) are the numbers of \( \alpha \) and \( \beta \) valence electrons, respectively. Some of the energies have also been calculated by the G3SX composite method\textsuperscript{30} with the geometries optimized at the B3LYP/6-31G(2df,p) level. Since the method does not include any empirical correction, this method has been proposed to apply for the system whose number of spins is changed like the present system. Therefore, we can compare the two composite schemes for the issue on the spin change. In addition, time-dependent density functional theory (TD-DFT)\textsuperscript{33–35} at the B3LYP/6-31+G(d) level has been used to calculate the vertical excitation energies and oscillator strengths for the \( S_1 \) and \( S_2 \) states of C\textsubscript{6}H\textsubscript{5}NO. The electronic structure calculations were carried out with the Gaussian 98\textsuperscript{36} and MOLPRO 98\textsuperscript{37} programs.

III. Results and Discussion

Dissociation of Nitrosobenzene at 248 nm. Ions of \( m/e \) = 30, 77, and 78 were the only fragments we observed from the photodissociation of nitrosobenzene at this wavelength. \( m/e \) = 78 is the corresponding \(^{13}\text{C}\) isotope of fragment \( m/e \) = 77. Photofragment ion images are shown in Figure 2a,b. Photolysis laser intensity in the region between 2.5 and 30 mJ/cm\textsuperscript{2} was used. They showed the same shapes of image. It suggests that one-photon absorption is the dominant process in this laser intensity region. Since there was no HNO and C\textsubscript{5}H\textsubscript{4} detected, we can conclude that there is only one dissociation channel at 248 nm, i.e., C\textsubscript{6}H\textsubscript{5}NO \( \rightarrow \) C\textsubscript{6}H\textsubscript{4} + NO, although the other channel, C\textsubscript{6}H\textsubscript{5}NO \( \rightarrow \) C\textsubscript{6}H\textsubscript{4} + HNO, is also energetically accessible (vide infra). As a result, nitrosobenzene is a “clean” precursor to generate phenyl radical at this wavelength.

The photofragment translational energy distribution obtained from the images is illustrated in Figure 2c. It shows that the probability monotonically decreases with increasing translational energy. The average released translational energy is about 6.9 kcal/mol, and it is about 11\% of the total available energy.
Figure 3. (a) Photofragment ion image intensity profiles of m/e = 77 from two different photolysis laser polarizations at 248 nm. Thick and thin lines represent the polarization of UV laser perpendicular and parallel to the VUV laser beam, respectively. (b) Anisotropy parameter β as a function of fragment translational energy. The dotted lines represent the upper and lower limits of the uncertainty.

Compared to the average translational energy measured in previous studies, our value is much smaller than 29% of the fragment translational spectroscopy measurement at photolysis wavelength 266 nm, and it is very close to 7.3% and 6–11% of velocity map ion imaging measurements at 290.5 and 225.96 nm, respectively.

The C₆H₅ photofragment ion image profiles at two different photolysis laser polarizations are presented in Figure 3a. The shapes and the intensities of the profiles at the polarization directions parallel and perpendicular to the VUV probe laser beam are very close to each other. The anisotropy parameter β for the fragments with different translational energy is illustrated in Figure 3b. In the low translational energy region where most of the fragments are produced, the values of β are very close to zero, indicating the isotropic distribution of the fragments. In the high translational energy region, the values of β fluctuate between 0 and 1. The poor S/N ratios are due to the small amount of high translational energy fragments produced in the high translational energy region. We can conclude that most of the fragments are isotropically distributed. If there is any anisotropic distribution, it must be from the fragments with large translational energy. However, the amount of those fragments is very small, and the value of β is positive.

The anisotropy parameter β we measured at 248 nm is very close to the value of 0.05 from the single line measurement at 225.96 nm. It is also very close to the value of 0.03–0.05 from the measurement of several rotational states of NO ν = 0 at photolysis wavelength 290.5 nm. However, it is very different from the value of −0.64 obtained from the photofragment translational energy measurement at 266 nm. Both the translational energy distribution and anisotropy parameter β measurement suggest that our results are similar to those of Dick and co-workers, but they are different from those of Han and co-workers.

The C₆H₅NO dissociation at 193 nm was found to be very similar to that at 248 nm. The C₆H₅ photofragment ion image intensity profiles at two different photolysis laser polarizations were found to be very close to each other, as presented in Figure 6a. The values of β as a function of translational energy are shown in Figure 6b. It suggests that most of the fragments are isotropically distributed, and only a small amount of fragments with large translational energy have a positive value of β. The dissociation mechanism at 193 nm must be similar to that at 248 nm.

Decomposition of Phenyl Radical. The phenyl radical plays a very important role in the combustion of small aromatic hydrocarbons. There has been considerable interest in its reactions with combustion species as well as its decomposition kinetics and mechanism. The ab initio calculation of a previous study showed that the decomposition of phenyl radical...
producing benzyne + H was endothermic by 76.0 kcal/mol, and the reaction was reported to occur without a distinct transition state based on geometry optimization with the B3LYP method. This loose structure, also confirmed by MP2 and CCSD optimizations with the 6-31+G(d,p) basis set, however, overestimated the high-temperature thermal decomposition rate constant determined by Braun-Unkoff et al., as was also shown by Wang et al. The new optimization carried out in this work by the G96LYP/6-31+G(d,p) method located a low-energy transition state. A G2M calculation based on this structure gives the barrier for the decomposition reaction at 79.4 kcal/mol above C₆H₅. For phenyl radicals produced from the photodissociation of nitrosobenzene at 193 nm, the maximum internal energy for phenyl radical is 93.8 kcal/mol (experimental value from NIST chemistry webbook). The decomposition into benzyne + H therefore is energetically allowed, as shown in Figure 7.

Figure 5. Fragment ion image intensity profiles at various delay times. The thin and thick lines represent m/e = 77 and 76, respectively. (a) t = 5 μs, (b) t = 9 μs, (c) t = 15 μs, (d) t = 18 μs.

Figure 6. (a) Photofragment ion image intensity profiles of m/e = 77 from two different photolysis laser polarizations at 193 nm. Thick and thin lines represent the polarization of UV laser perpendicular and parallel to the VUV laser beam, respectively. (b) Anisotropy parameter β as a function of fragment translational energy. The dotted lines represent the upper and lower limits of the uncertainty.

Figure 7. Energy level scheme from the TD-DFT calculations at the B3LYP/6-31+G(d) level and schematic energy diagram for the isomerization and dissociation reactions of C₆H₅NO calculated at the G2M(RCC, MP2)//B3LYP/6-31+G(d) level in kilocalories per mole. Note that the energy of the 1A’ state, 35.3 kcal/mol, includes ZPE correction. The energy levels in parentheses are from ref 18.
of phenyl radicals can be seen from the fast rise of the central part of the image \( m/e = 76 \) at short delay time. On the other hand, phenyl radicals located on both sides contain less internal energy, and they have slow decomposition rates. The corresponding benzene only appears at long delay time images. For the phenyl radicals positioned at both ends of the image in velocity axis, the translational energy released is large and the energy left in the internal degrees of freedom is too small for the radical to be further dissociated into benzene and H atom. They remain as phenyl radicals and no analogous benzene is produced. Therefore, the length of the image \( m/e = 76 \) is shorter than that of \( m/e = 77 \) even at very long delay times.

The decomposition rate of phenyl radical as a function of internal energies can be obtained from the image intensity changes of each part of the image along the fragment velocity axis at various delay times. The internal energy of phenyl radical can be calculated from

\[
E\text{(int)}_{\text{phenyl}} = h\nu - D_0 - E\text{(tran)} - E\text{(int)}_{\text{NO}}
\]

The photon energy \( h\nu \) is 148 kcal/mol, the dissociation energy \( D_0 \) is 54 kcal/mol, and the amount of translational energy released, \( E\text{(tran)} \), can be calculated directly by use of the fragment velocity obtained from the image. The only uncertainty in this equation is the internal energy of fragment NO. However, a proper estimation of the NO fragment internal energy could be made according to the previous studies and our measurement. Previous studies showed that the rotational and vibrational state distributions of NO fragments are statistical, and most of the energy is located in phenyl radical vibrational degrees of freedom. For example, the average vibrational energy of NO fragment is only 1.3% of the total available energy at photolysis laser wavelength 255 nm, and the rotational energies of both phenyl radical and NO are only 0.2% and 3.7%, respectively due to the transition-state geometry. For nitrosobenzene photodissociation at 193 nm, both the value of anisotropy parameter \( \beta \) and the translational energy distribution suggest that the dissociation mechanism is similar to that at 255 nm, i.e., the dissociation occurs after internal conversion to the lower electronic state. Energy must be redistributed among various vibrational degrees of freedom before dissociation occurs and the energy distribution is statistical. Therefore, we estimated that about 95% of the available energy (total available energy after the subtraction of translational energy) is distributed in phenyl radical vibrational degrees of freedom.

For a given internal energy, the decomposition of phenyl radical into benzene and H atom can be described by \( m_{77}(T_1) = \exp(-kT_1) \) and the growth of the corresponding benzene can be described by \( m_{76}(T_1) = 1 - \exp(-kT_1) \). \( m_{77}(T) \) is the phenyl radical concentration for a given internal energy at delay time \( T \), \( m_{76}(T) \) is the benzene concentration produced from the corresponding phenyl radical. \( k \) is the dissociation rate of phenyl radical. The ion intensity of \( m/e = 77 \) and 76 thus can be described by

\[
I_{m77}(T_1) = A(1 - \gamma) \exp(-kT_1) \quad (1)
\]

\[
I_{m76}(T_1) = B[1 - \exp(-kT_1)] + A\gamma \exp(-kT_1) \quad (2)
\]

A and B are the ionization cross sections of fragment mass 77 and 76, respectively. \( \gamma \) is the branching ratio of benzene produced from the dissociative ionization of phenyl radical, described by

\[
C_6H_5 + h\nu_{\text{VUV}} \rightarrow C_6H_4^+ + H(3)
\]
TABLE 1: Relative Energies for the Isomerization and Decomposition Reactions of C₆H₅NO

<table>
<thead>
<tr>
<th>species or reaction</th>
<th>B3LYP/6-31G(d)</th>
<th>G2M</th>
<th>B3LYP/6-31+G(d)</th>
<th>G2M</th>
<th>B3LYP/6-31G(2df,p)</th>
<th>G3SX</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₆H₅NO</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>C₆H₅ + NO</td>
<td>53.3</td>
<td>56.5</td>
<td>52.2</td>
<td>56.6</td>
<td>53.0</td>
<td>55.6</td>
</tr>
<tr>
<td>TS</td>
<td>66.1</td>
<td>66.7</td>
<td>65.6</td>
<td>66.6</td>
<td>63.3</td>
<td>66.0</td>
</tr>
<tr>
<td>C₆H₄N(H)O</td>
<td>60.5</td>
<td>60.2</td>
<td>57.8</td>
<td>60.3</td>
<td>58.4</td>
<td>59.6</td>
</tr>
<tr>
<td>C₆H₅ + HNO</td>
<td>96.2</td>
<td>86.2</td>
<td>93.2</td>
<td>86.2</td>
<td>94.8</td>
<td>86.3</td>
</tr>
<tr>
<td>C₆H₅ + H + NO</td>
<td>140.4</td>
<td>134.0</td>
<td>138.4</td>
<td>134.0</td>
<td>140.2</td>
<td>134.1</td>
</tr>
</tbody>
</table>

Relative energies are ZPE-corrected in kilocalories per mole. Based on the optimized geometries calculated at B3LYP/6-31G(d), B3LYP/6-31+G(d), and B3LYP/6-31G(2df,p), respectively.

TABLE 2: Vertical Energies and Oscillator Strengths (f) for C₆H₅NO, Estimated by TD-DFT at the B3LYP/6-31+(d) Level

<table>
<thead>
<tr>
<th>state</th>
<th>sym</th>
<th>B3LYP/6-31+G(d)</th>
<th>experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td>S₁</td>
<td>1A</td>
<td>35.9 (0.0003)</td>
<td>32.9</td>
</tr>
<tr>
<td>S₂</td>
<td>1A</td>
<td>90.4 (0.0183)</td>
<td>89.3</td>
</tr>
</tbody>
</table>

Vertical energies are given in kilocalories per mole; oscillator strengths are shown in parentheses. From ref 18.

Figure 9. Optimized structures of the reactant, transition state, and intermediate at the B3LYP/6-31+G(d) level of theory.

Table 3: Decay Rate of C₆H₅NO via Different Pathways

<table>
<thead>
<tr>
<th>pathway</th>
<th>248 nm</th>
<th>193 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₆H₅NO → C₆H₅ + NO</td>
<td>2.5 × 10⁻⁶</td>
<td>3.2 × 10⁻⁶</td>
</tr>
<tr>
<td>C₆H₅NO → C₆H₄ + HNO</td>
<td>1.0 × 10⁻⁶</td>
<td>1.3 × 10⁻⁷</td>
</tr>
<tr>
<td>C₆H₅NO → C₆H₄N(H)O</td>
<td>2.9 × 10⁻⁴</td>
<td>1.8 × 10⁻⁷</td>
</tr>
</tbody>
</table>

The rate constant for C₆H₅NO → VTS → C₆H₄ + HNO with VTS as the limiting step.

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</table>

The rate constant for C₆H₅NO → VTS → C₆H₄ + HNO with VTS as the limiting step.

by use of the Variflex code. The minimum energy paths (MEP) representing the dissociation processes were approximated with the Varshni potential, and the optimized geometries were used to calculate the barrier heights and energy gaps between the reactant and transition state at the TD-DFT level. The resulting barrier heights are given in Table 2.

As shown in Table 1, the energetics predicted by both G2M and G3SX agree very closely. The latter, which does not include “high-level corrections”, is believed to be more reliable for applications to reactions with spin changes. In Table 2, the result of our TD-DFT calculations at the B3LYP/6-31+G(d) level for the S₁ and S₂ states confirm the energy gap between them, 54.5 kcal/mol, which compares closely with the experimental value, 56.4 kcal/mol.¹⁸

(2) Decomposition of Photoexcited C₆H₅NO. Assuming that the internal conversion is fast comparing with fragmentation lifetimes, we can predict the fragmentation rates of C₆H₅NO following the excitation at 248 and 193 nm on the basis of the RRKM theory. As both product channels giving NO and HNO occur barrierlessly, the energy-dependent specific constants (kₑ) were evaluated with the flexible transition state approach.⁴⁴-⁴⁷

![Diagram](Image)
three MEPs producing NO. The thermal unimolecular dissociation rate constant defined by

$$\frac{d[C_6H_5NO]}{dt} = k^\infty [C_6H_5NO]_0 = \sum k^\infty_i \chi_i = k^\infty_X[A] + k^\infty_A[B]$$ (5)

where $[C_6H_5NO]_0$, [X], [A], and [B] are, respectively, the initial concentration of nitrosobenzene entirely at its ground electronic state and those at the ground electronic, 1$\AA^*$, and 1$\AA''$ states under thermal equilibrium, and the $k^\infty_i$ are the first-order rate constants for the dissociation from these states. Assuming $K_A$ and $K_B$ to be the equilibrium constants for X $\leftrightarrow$ A and X $\leftrightarrow$ B, respectively, eq 5 leads to the total unimolecular rate constant:

$$k^\infty = (k^\infty_X + k^\infty_A K_A + k^\infty_B K_B)/(1 + K_A + K_B)$$ (6)

The predicted individual rate constants presented in Figure 10 gave $k^\infty = 1.52 \times 10^{17}$ exp[$-55 200/RT$] s$^{-1}$, which is in excellent agreement with the result obtained by Park et al.,$^{30}$ $k^\infty = (1.42 \pm 0.13) \times 10^{17}$ exp[$-(55 060 \pm 1080)/RT$] s$^{-1}$, confirming the unusually high A-factor. Notably, the result presented in Figure 10 indicates that the contributions from both $T_1$ and $S_1$ states are insignificant in the present system. For the decomposition of SO$_2$ at high temperatures in shock waves, we have recently shown that contributions from three excited states to its second-order rate constants are significant.$^{52}$

IV. Conclusions

We demonstrate that there is only one dissociation channel of nitrosobenzene at both 248 and 193 nm. No products corresponding to the dissociation channel of C$_6$H$_5$NO $\rightarrow$ C$_6$H$_5$ + HNO were observed, in full agreement with theoretical prediction. The dissociation rate of nitrosobenzene is on a time scale much longer than the rotation of molecule, and the fragment distribution is almost isotropic. The results at 248 nm are close to the measurement of Dick and co-workers. In addition, about 10% of phenyl radical produced at 193 nm further decompose into benzyne and H atom, and the dissociation rates of phenyl radical as a function of internal energies were measured. The results for the dissociation of the excited C$_6$H$_5$NO and the C$_6$H$_5$ radical agree well with theoretically predicted values. In addition, the rate constant for the thermal decomposition of nitrosobenzene has been calculated with variational RRKM theory by including the small contributions from the two low-lying excited states (T$_1$ and S$_1$). The agreement between theory and the experiment of Park et al.$^{30}$ was also found to be excellent, confirming for the first time the observed very high A-factor ($>10^{17}$ s$^{-1}$).

Acknowledgment. C.K.N. acknowledges the support from the National Science Council, Taiwan, under Contract NSC 91-2113-M-001-023. M.C.L. and Y.M.C. are grateful to Dr. J. Park for his preliminary optimization of the TS in Figure 7 and for the support of this work from the Basic Energy Sciences, Department of Energy, under Contract DE-FG02-97-ER14784, and the Cherry L. Emerson Center of Emory University for the use of its resources, which are in part supported by a National Science Foundation grant (CHE-0079627) and an IBM shared University Research Award. M.C.L. also acknowledges the support from the National Science Council for a Distinguished Visiting Professorship at National Chiao Tung University in Hsichiu, Taiwan.

References and Notes

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(49) Varshni, Y. P. Rev. Mod. Phys. 1957, 29, 664.

