seconds to evolve, and the rates of secondary electron interactions can be observed in a few Torr of these gases. As a result of these interactions, the secondary and subsequent generations of electrons produced from primary ionization events are degraded by inelastic processes until they become subexcitation electrons. Further energy loss by momentum transfer (elastic collisions) processes results in thermalization of the electrons.

These experiments have clearly shown the time scale for the degradation of epithermal electron to subexcitation energies in pure rare gases. The results provide a new opportunity for comparison with theoretical calculations, which are in progress and qualitatively agree with the observations presented here.<sup>7,8</sup>

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## Energy Transfer in the Infrared Laser-Induced Reaction of Methyl Isocyanide

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Experimental results are presented for the infrared laser-induced isomerization of methyl isocyanide to acetonitrile in the presence of several bath gases: Ar, O<sub>2</sub>, CO<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>5</sub>CN, C<sub>2</sub>H<sub>5</sub>NC, and di-*tert*-butyl peroxide (DTBP). For all addends except DTBP, increasing the bath gas pressure results in a decrease in acetonitrile yield due to collisional deactivation of the methyl isocyanide. The efficiency of this collisional deactivation is related to the heat capacity and to the vibrational mode distribution of the buffer gas. Ethyl isocyanide as a buffer gas shows an enhanced suppression of the acetonitrile yield due to moderation of the radical channel for the reaction. DTBP, on the other hand, increases the acetonitrile yield and lowers the threshold for massive isomerization due to its generation of methyl radicals.

#### Introduction

Infrared laser-induced chemistry has developed significantly since the demonstration of laser isotope separation in the 1970s.<sup>1,2</sup> In particular, it has been reported that for many systems, the reaction yield increases with pressure. Although a majority of these are well understood in terms of collisional hole-filling,<sup>3-12</sup> there are some notable exceptions. The most dramatic of these exceptions are the isomerization reaction of methyl isocyanide13 and ethyl isocyanide.<sup>14</sup> For both isocyanides there is a sharp, fluence-dependent, threshold pressure,  $P_{\mathcal{F}}$ , above which nearly complete isomerization occurs in a single pulse. (For a discussion of  $P_{\mathcal{F}}$ , see ref 13 and 14.) Below  $P_{\mathcal{F}}$  the conversion to the corresponding cyanide increases with reactant pressure to about 0.2%of the reactant per pulse before massive isomerization is observed. Although previous results have shown that this pressure dependence cannot be accounted for by a thermal explosion,13 understanding the pressure dependence of these reactions remains incomplete. In addition to its significance for laser-induced chemistry, the methyl isocyanide isomerization is a prototype for unimolecular reaction theories. Therefore understanding its collisional energy transfer is of broad interest.

Since, below  $P_3$ , the isomerization yield increases with pressure for pure methyl isocyanide,<sup>13</sup> the effect of several bath gases on the yield was examined. These include nonpolar addends Ar, O<sub>2</sub>,  $CO_2$ ,  $CH_4$ , and  $C_2H_6$ , polar addends ethyl cyanide and ethyl isocyanide, and two interactive addends ethyl isocyanide and di-tert-butyl peroxide (DTBP). The nonpolar addends were chosen because they are nonreactive, are representative of a range of vibrational degrees of freedom and heat capacities, and are transparent at the irradiation wavelength. Ethyl cyanide was used

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because of its similarity to ethyl isocyanide, and ethyl isocyanide was chosen because its isomerization energetics are very similar to those of methyl isocyanide. Finally, DTBP was added as a methyl radical generator.<sup>15</sup> Like the nonpolar addends, the latter three are transparent at the irradiation wavelength.

The results show that with the exception of DTBP, an increase in the pressure of the addend lowers the isomerization yield for a given reactant pressure and raises  $P_{\mathcal{F}}$ . For the nonpolar addends, the efficiency of this collisional quenching is related to the density of states of the addend. Comparison of ethyl cyanide and ethyl isocyanide reveals that the isocyanide is a more efficient quencher. Finally, DTBP is the only addend studied that lowers  $P_{3}$ .

The experimental setup for this work is described in the next section of this paper. The third section contains a presentation

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**Figure 1.** Acetonitrile yield as a function of addend partial pressure. Irradiation conditions: 11.8 Torr of methyl isocyanide, incident fluence  $2.7 \pm 0.1 \text{ J/cm}^2$  per pulse, 50 pulses,  $P_{\mathcal{F}} = 12.5 \pm 0.3$  Torr. (a)  $O_2$ ,  $C_2H_6$ , Ar, and  $CO_2$ ; (b)  $CO_2$  (repeated for reference) and  $CH_4$ .

of the results, the fourth section a discussion of the results, and the fifth section a summary.

### **Experimental Section**

The details of the experimental setup have been described earlier.<sup>13,14,16,17</sup> For the reported experiments, methyl isocyanide was irradiated with the 10P(20), 944.19 cm<sup>-1</sup>, transition of the CO<sub>2</sub> laser. All the buffer gases used are transparent at this wavelength, which excites the  $\nu_4$  band of methyl isocyanide. Except for the experiments with DTBP as the addend, product yield was determined as a function of addend gas partial pressure with a fixed methyl isocyanide partial pressure of 11.8 Torr. For the DTBP experiments, 0.7 Torr of DTBP was added and the methyl isocyanide partial pressure was varied to determine  $P_3$ , products, and relative product yield. For all experiments, the laser fluence was  $2.7 \pm 0.1 \text{ J/cm}^2$ . At this fluence,  $P_3$  for pure methyl isocyanide is  $12.5 \pm 0.3$  Torr. Sub- $P_3$  pressure samples were irradiated with 50 pulses. In addition,  $P_3$  was determined for 3 Torr of added argon or ethane.

Nondestructive preirradiation analysis was performed with an IBM instruments Model 85 FTIR. Postirradiation analysis was performed with a Hewlett-Packard 5750 gas chromatograph, a Hitachi-Perkin-Elmer Model RMU-6 mass spectrometer, and/or a Hewlett-Packard Model 5992-A GC-MS.

Argon and oxygen were obtained from Middlesex Welding Supply Co., methane (CP grade) from Matheson Gases. These were used without further purification. Ethane (CP grade) was obtained from Union Carbide Corp.,  $CO_2$  (grade 4) from Airco Industrial Gases, DTBP from Pfaltz and Bauer, and ethyl cyanide (99% pure) from Aldrich Chemical Co. These last four were degassed and transferred on a vacuum line. Methyl isocyanide and ethyl isocyanide were synthesized according to the method of Casanova et al.,<sup>18</sup> with the modifications reported earlier.<sup>13</sup>



Figure 2. Yield as a function of added ethyl cyanide or ethyl isocyanide partial pressure. Irradiation conditions: 11.8 Torr of methyl isocyanide, incident fluence  $2.7 \pm 0.1 \text{ J/cm}^2$ , 50 pulses,  $P_{\mathcal{F}} = 12.5 \pm 0.3 \text{ Torr}$ .

 TABLE I: Heat Capacity and Collisional Efficiency Data for Addend Gases

| addend                           | С <sub>р,300 К</sub> , <sup>а</sup><br>cal mol <sup>-1</sup> К <sup>-1</sup> | $C_{p,800 \text{ K}},^{a}$<br>cal mol <sup>-1</sup> K <sup>-1</sup> | $\beta_p^c$ | $\beta_{\mu}{}^{c}$ |
|----------------------------------|--|---|-------------|---------------------|
| Ar                               | 4.97   |   | 0.136       | 0.135               |
| $O_2$                            | 7.017  | 7.29  |             |                     |
| $CO_2$                           | 8.874  | 11.409  | 0.32        | 0.33                |
| CH₄                              | 8.536  | 15.2  | 0.44        | 0.33                |
| $C_2H_6$                         | 12.5   | 25.83   | 0.56        | 0.52                |
| CH <sub>3</sub> NC               | 12.83  | 21.34   |             |                     |
| C <sub>2</sub> H <sub>5</sub> CN | 17.30  | 32.7  |             |                     |
| C <sub>2</sub> H <sub>5</sub> NC | d  | d   |             |                     |

<sup>a</sup>References 27-29. <sup>b</sup>Reference 22. <sup>c</sup>Reference 24. <sup>d</sup>Assume values for ethyl cyanide; see ref 29.

**TABLE II: Dipole Moments of Some Compounds** 

| compd              | dipole moment, D   | compd                            | dipole moment, D              |
|--------------------|--------------------|----------------------------------|-------------------------------|
| CH <sub>3</sub> CN | $3.92 \pm 1\%^{a}$ | C <sub>2</sub> H <sub>5</sub> CN | $4.02 \pm 1\%^{a}$            |
| CH₃NC              | $3.85 \pm 2\%^{a}$ | C <sub>2</sub> H <sub>5</sub> NC | 3.5 (in benzene) <sup>b</sup> |

<sup>a</sup> Reference 28. <sup>b</sup> Reference 30.

According to gas chromatographic analysis, the methyl isocyanide was better than 99.5% pure and the ethyl isocyanide was better than 99.0% pure.

#### Results

With the exception of DTBP, the products observed following irradiation of a sample of pure methyl isocyanide or a mixture are the same. The acetonitrile yield, however, decreases with increasing addend partial pressure. Typical data for the yield as a function of addend partial pressure are shown in Figure 1 and 2, where the incident fluence is  $2.7 \pm 0.1 \text{ J/cm}^2$ . With this fluence,  $P_{\mathcal{F}}$  for pure methyl isocyanide is  $12.5 \pm 0.3$  Torr. In addition to suppressing the acetonitrile yield, increasing the addend partial pressure increases  $P_{\mathcal{F}}$ . For example, 3 Torr of argon raises the methyl isocyanide  $P_{\mathcal{F}}$  from  $13.0 \pm 0.2$  to  $13.8 \pm 0.3$  Torr, while 3 Torr of ethane raises it to  $17.3 \pm 0.3$  Torr.<sup>16</sup>

Figure 2 shows that of the two addends with a permanent dipole, ethyl isocyanide suppresses the acetonitrile yield more than ethyl cyanide does. These two addends have very similar heat capacities, vibrational complexities, and dipole moments (Tables I and II). The major difference between them is that ethyl isocyanide isomerizes while ethyl cyanide does not. Therefore, both the ethyl cyanide and the total nitrile partial pressure were examined as a function of the ethyl isocyanide addend partial pressure. These results are shown in Figure 3.

Samples containing DTBP were very different. DTBP is the only addend studied that lowers  $P_3$ . For example, 0.7 Torr of DTBP lowers  $P_3$  from 12.7  $\pm$  0.2 to 10.8  $\pm$  0.2 Torr.<sup>19</sup> In addition

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Figure 3. Ethyl cyanide, acetonitrile, and total nitrile partial pressure as a function of ethyl isocyanide initial partial pressure.

to the normal products, acetone was also observed among the products.  $^{19}\,$ 

Since this reaction is highly fluence dependent,<sup>20</sup> the effect of addends at both higher and lower fluence was examined. It was found that the yield dependence on both the addend pressure and the nature of the addend is retained.

#### Discussion

Generally, when a buffer gas is added to a substrate, the product yield either rises owing to a collisional hole-filling or falls owing to deactivating energy transfer. The observed decrease in yield with increasing addend pressure indicates that with the exception of DTBP, the major role of substrate-addend collisions is deactivation. This lack of hole-filling is consistent with two other results: (1) the adherence to Beer's law for the pressures of methyl isocyanide<sup>13</sup> and buffer gas used here<sup>17</sup> and (2) the small anharmonicity of the methyl isocyanide mode excited.<sup>20</sup>

The most remarkable feature of this deactivation is its insensitivity to many parameters associated with collisional activation such as the collision cross section  $(s^2)$  or the reduced mass  $(\mu)$ .<sup>21</sup> In the following discussion, we will show that the parameter that governs the deactivation is the heat capacity of the mixture (referred to as the system heat capacity).

Nonpolar Addends. The results for nonpolar addends (Figure 1) indicate that substrate-addend collisions are deactivating and hence quench the isomerization reaction. In addition, on a percollision basis, the larger, more complex colliders quench more effectively. In fact, the decrease in acetonitrile production seems to be inversely related to the heat capacity. This is not unreasonable since the methyl isocyanide is the only material receiving energy in the irradiation. The addend acquires energy only by collision with the reactant and therefore remains energetically cold. When the excited methyl isocyanide collides with the addend, the addend absorbs a part of the energy in proportion to its heat capacity. In fact, if the acetonitrile yield is examined not as a function of addend pressure but rather of system heat capacity (Figure 4), all addends except argon quench with the same efficiency. Argon is a significantly less efficient quencher.

It is reasonable that argon is less efficient in this energy-transfer process since it does not vibrate. Furthermore, results from the remaining addends indicate that it is the presence of vibrational modes that is critical. The remaining addends, which have a range of vibrational complexities and heat capacities that have widely different temperature dependencies,<sup>22</sup> all quench with the same efficiency (Figure 4). This is also reasonable since, in general, the efficiency of collisional energy transfer is much higher if the



Figure 4. Acetonitrile yield as a function of the system heat capacity: (a)  $O_2$ ,  $C_2H_6$ , Ar, and  $CO_2$ ; (b)  $CO_2$  (repeated for reference) and  $CH_4$ . Irradiation conditions are as in Figure 1.

modes of the colliders are closer in energy.

Earlier results have shown that  $P_{\mathcal{F}}$  is dependent on the level of excitation.<sup>20</sup> Therefore, the relationship between deactivation efficiency and the change in  $P_{\mathcal{F}}$  was examined. It is found that all nonpolar addends raise  $P_{\mathcal{F}}$ . Furthermore, the increase in  $P_{\mathcal{F}}$ is consistent with the quenching efficiency in the subthreshold yield.

Thus, the ability of an addend to deactivate methyl isocyanide is related to its heat capacity and to its vibrational complexity. This relationship is consistent with that observed by Rabinovitch and co-workers in the complementary thermal experiments.<sup>23,24</sup> In the laser experiments, only methyl isocyanide receives energy from the laser radiation, and collisions with the addend serve to redistribute this energy. In the thermal experiments conducted by Rabinovitch et al., methyl isocyanide is present in low concentration (12 mTorr), while the addend is in large excess (5-300-fold), and the entire system is kept in thermal equilibrium. Hence, collisions with the addend serve to activate methyl isocyanide. The two experiments are, therefore, complementary with the most efficient activator in the thermal work expected to be the most efficient quencher in the laser work. Indeed, Table I indicates that there is a good correlation of the heat capacity with the activation efficiency  $(\beta_p)$ . Thus, both the vibrational modes and the heat capacity of the addend determine the quenching efficiency.

In another related work, Shaw and Pritchard<sup>25</sup> studied the photochemical isomerization of methyl isocyanide with argon, oxygen, and ethane as buffer gases. Methyl isocyanide was excited with ultraviolet, 253.7-nm, radiation, while the buffer gases were

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Figure 5. Acetonitrile yield as a function of the system heat capacity (heat capacity of the mixture) for the addends ethyl isocyanide and ethyl cyanide. Irradiation conditions are as in Figure 2.

initially "cold". Their work shows that increasing the buffer gas pressure results in a decrease in the isomerization rate. For example, for a reactant pressure of 1 Torr, 200 Torr of either argon or ethane decreases the rate by a factor of 10. However, among argon, oxygen, and ethane, oxygen is dramatically more efficient in reducing the extent of reaction; 20 Torr of oxygen completely quenches the isomerization. In contrast, this exceptionally high efficiency for oxygen is generally an efficient deactivator for molecules in the triplet state, the ultraviolet photochemical isomerization undoubtedly involves a triplet state while the infrared laser-induced reaction does not.

*Polar Addends*. Since methyl isocyanide has a fairly large dipole moment (see Table II), the cross section for collisions between it and other compounds having permanent dipoles is larger than the cross section for collision with nonpolar molecules due to the long-range dipole-dipole interaction. If this larger cross section results in a more efficient energy transfer, then the suppression of the acetonitrile yield should be greater. The data in Figure 2, however indicate that ethyl cyanide and ethyl isocyanide fit the same general description as the nonpolar addends. That is, there is no enhanced quenching due to the presence of the dipole moment. This is an important finding because it allows a detailed comparison of the results for addition of ethyl isocyanide to those for addition of ethyl cyanide.

*Reactive Addend. Ethyl Isocyanide.* The significance of the result of addition of ethyl isocyanide is most easily understood if it is compared with that for addition of ethyl cyanide. Figure 2 shows the subthreshold yield as a function of addend pressure, and Figure 5 shows the yield as a function of system heat capacity. Both figures indicate that ethyl isocyanide is a more efficient quencher than ethyl cyanide. Since both compounds have very similar dipole moments (Table II), heat capacities (Table I), and vibrational modes, this difference must be due to the isomerization of ethyl isocyanide compared to the nonreactivity of ethyl cyanide. Furthermore, this isomerization must interact with the methyl isocyanide isomerization to moderate the methyl isocyanide reaction rate. There are two possibilities for this: by reducing the temperature or by interfering with the radical channel.<sup>19</sup> These alternatives will be examined in turn.

In these experiments, methyl isocyanide is the only material receiving energy from the laser radiation. The addends receive energy through collisions with the methyl isocyanide, resulting in a lower temperature for the mixture than for a sample of pure methyl isocyanide. Furthermore, this effect will be the same for both ethyl isocyanide and ethyl cyanide since their heat capacities are the same. If the isomerization of the heated ethyl isocyanide results in an additional lowering of the temperature, this would explain the lower acetonitrile yield in the presence of ethyl isocyanide compared with that of ethyl cyanide.

However, as shown below, the ethyl isocyanide isomerization will *raise* the temperature. This is understood by comparing the isomerization energetics of ethyl isocyanide to those of methyl isocyanide. For unimolecular isomerization, the activation energies, preexponential factors, and stabilization energies for ethyl isocyanide and methyl isocyanide are essentially the same.<sup>26</sup> The major difference between the two isocyanides is that the highpressure limit for ethyl isocyanide is lower than that of methyl isocyanide. (At the pressures used here, 10-15 Torr, ethyl isocyanide has reached its high-pressure limit, while methyl isocyanide is significantly below.<sup>24</sup>) The energy that ethyl isocyanide receives from methyl isocyanide in these experiments will result, at least partially, in isomerization so that the stabilization energy will be returned. Furthermore, the rate of this return is greater than that of the methyl isocyanide isomerization due to the pressure dependence of the rate constant. The ethyl isocyanide isomerization should, therefore, contribute to the heating of the sample. If a completely thermal description were applicable, ethyl isocyanide would be expected to suppress the acetonitrile yield less than, or at most, the same as ethyl cyanide. Since the opposite effect is observed, an additional reaction channel must be present.

This additional channel is the radical channel suggested previously.<sup>19,24</sup> Ethyl isocyanide interacts with this channel as

$$CH_3^{\bullet} + CH_3NC \rightarrow CH_3CN + CH_3^{\bullet*}$$
(1)

$$CH_3^{\bullet} + C_2H_5NC \rightarrow CH_3CN + C_2H_5^{\bullet}$$
 (2)

$$C_2H_5 + CH_3NC \rightarrow C_2H_5CN + CH_3$$
(3)

$$C_2H_5 + C_2H_5NC \rightarrow C_2H_5CN + C_2H_5 *$$
 (4)

where an asterisk indicates a radical of higher energy than its precursor. Since the ethyl radical is more stable, i.e., longer lived, than the methyl radical, the net effect is a moderation of the radical channel of the methyl isocyanide isomerization. Hence, not only is the direct yield from this channel reduced, but also the rate of energy liberation is slowed, reducing the thermal isomerization rate. The net result is a lower yield with ethyl isocyanide as an addend compared to that with ethyl cyanide.

The results shown in Figure 3 indicate that the ethyl isocyanide addend does indeed isomerize. Furthermore, the partial pressure of the ethyl cyanide product increases with increasing ethyl isocyanide initial partial pressure. This increased ethyl cyanide production comes at the expense of that of acetonitrile, with the combined nitrile yield showing a moderate decrease with increasing ethyl isocyanide initial partial pressure. The decrease in the combined nitrile yield may be understood as follows: As more ethyl isocyanide is added, the system heat capacity increases. Since the ethyl isocyanide is transparent, it is energetically cold, and the resulting initial temperature is lower, which results in a decreased combined nitrile yield. The ethyl cyanide partial pressure increases both because ethyl isocyanide is nearer its high-pressure rate constant at these pressures and because ethyl isocyanide is a reasonably efficient methyl radical trap and the resulting ethyl radical is more stable.

Reactive Addends. DTBP. The effect of addition of DTBP to methyl isocyanide has been discussed in a previous paper;<sup>19</sup> therefore, only a brief discussion will be given here. The heat capacity of DTBP is very much larger than any other addend examined. Therefore, if it were totally nonreactive, it would completely quench the isomerization of the methyl isocyanide and raise  $P_{\mathcal{F}}$  enormously. Since DTBP does react, it is important to examine its reaction energetics.<sup>19</sup> Although the decomposition reaction of DTBP is exothermic, its much larger heat capacity results in a smaller contribution to the sample temperature change

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than the methyl isocyanide reaction. Hence, like ethyl isocyanide, DTBP should suppress the acetonitrile yield and raise  $P_{\mathcal{T}}$ . Only because, in the course of the reaction, DTBP produces methyl radicals does it enhance the acetonitrile yield and lower  $P_{\mathcal{T}}$ . This lowering of  $P_{\mathcal{F}}$  is significant with only 0.7 Torr of DTBP lowering the threshold by 2 Torr.

#### Summary

The effect of nonpolar bath gases on the methyl isocyanide isomerization is to decrease the yield of acetonitrile in the subthreshold region and to increase  $P_{\mathcal{F}}$ . It is found that the greater the partial pressure of a particular bath gas, the lower the yield. Results also indicate that the degree of suppression of the acetonitrile yield is related to the heat capacity of the addend and to the vibrational modes in the addend. These findings support the conclusion that rotational hole-filling is not significant in the reaction.

It is also found that addition of polar addends fits the same general description as the nonpolar addends. The two reactive addends, however, show different effects. Ethyl isocyanide shows an enhanced suppression of the acetonitrile yield due to its moderation of the radical reaction channel. Addition of DTBP, on the other hand, increases the acetonitrile yield and lowers  $P_{\mathcal{F}}$ by introducing methyl radicals into the system, thus enhancing the radical channel.

In conclusion, the primary effect of methyl isocyanide-addend collisions is to redistribute the energy and deactivate the methyl isocyanide.

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Registry No. DTBP, 110-05-4; methyl isocyanide, 593-75-9; ethyl isocyanide, 624-79-3.

# Theoretical Studies of the Insertion Reactions of Atomic Carbon and Silicon into Methane and Silane

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The mechanisms for the insertions of atomic (<sup>1</sup>D and <sup>3</sup>P) carbon and silicon into the C-H and Si-H bonds of methane and silane are investigated by ab initio SCF methods, many body perturbation theory, and a localized molecular orbital (LMO) analysis. The LMO analysis shows that the insertion of  ${}^{1}D$  atoms into CH<sub>4</sub> and SiH<sub>4</sub> may be classified into two types: cationic hydrogen transfer and anionic hydrogen transfer. For the triplet atoms the LMO analysis suggests two different insertion reaction mechanisms: the near abstraction and the pull-push mechanisms.

#### I. Introduction

The chemical reaction mechanisms for the reactions of atoms are a very active area for both experimental and theoretical investigations. For example, experimental studies of the reaction of atomic carbon with molecular hydrogen have shown the reaction to be very fast,<sup>1</sup> while ground-state <sup>3</sup>P carbon is essentially unreactive<sup>1</sup> with CH<sub>4</sub>. It is known that atomic carbon reacts with saturated substrates through two primary mechanisms:<sup>2</sup> insertion and hydrogen abstraction.

The first theoretical study of the reaction of atomic carbon with molecular hydrogen was reported by Blint and Newton.<sup>3</sup> They found that the insertion of <sup>1</sup>D carbon follows a perpendicular  $(C_{2n})$ minimum energy path with no energy barrier. For <sup>3</sup>P carbon, formally a thermally forbidden process, there are two surfaces relevant to this reaction in the  $C_{2\nu}$  approach: The  ${}^{3}A_{2}$  surface is lower in energy at large C-H<sub>2</sub> separations, while the  ${}^{3}B_{1}$  surface leads to the ground state of CH<sub>2</sub> with a large (91.7 kcal/mol) energy barrier. There is an avoided intersection of the  ${}^{3}A_{2}$  and  ${}^{3}B_{1}$  surfaces along the reaction path in C<sub>s</sub> symmetry.

The reaction mechanism for the insertion of <sup>1</sup>D carbon into molecular hydrogen may be understood by considering the interaction of the highest occupied (HOMO) and lowest unoccupied molecular orbitals (LUMO) for the atom and molecule, that is, in terms of a four-orbital, four-electron interaction. In this sense, the reaction mechanism is similar to that of the singlet carbene insertion into molecular hydrogen.<sup>4-10</sup> In the case of the reaction of atomic carbon with methane, the simplest saturated hydrocarbon, the symmetry is reduced to  $C_s$ . Whereas the least motion  $C(^{3}P) + H_{2}$  insertion reaction is symmetry forbidden, the  $C(^{3}P)$ + CH<sub>4</sub> insertion is formally allowed. Here again, the reaction  $C + CH_4$  can be compared to the analogous carbene insertion reaction. Also, the reactions of atomic carbon with silane, and of atomic silicon with methane and silane, are of interest in order to study the differences between carbon and silicon reactivity.

In this paper, we study the insertion reaction mechanisms for the following eight reactions:

> $C(^{1}D) + CH_{4} \rightarrow ^{1}HCCH_{3}$ (1)

 $C(^{1}D) + SiH_{4} \rightarrow ^{1}HCSiH_{3}$ (2)

- $Si(^{1}D) + CH_{4} \rightarrow ^{1}HSiCH_{3}$ (3)
- $Si(^{1}D) + SiH_{4} \rightarrow ^{1}HSiSiH_{3}$ (4)

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