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Pressure Effect on CH_3 and C_2H_3 Cross-Radical Reactions

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The effect of pressure on the cross-radical reactions of vinyl and methyl radicals has been investigated. These radicals were produced by excimer laser photolysis of methyl vinyl ketone ($CH_3COC_2H_3$) at 193 nm. The reaction products were detected and analyzed using a sensitive gas chromatograph and mass spectrometer. The study covered a pressure range from about 0.28 kPa (2.1 Torr) to 27 kPa (200 Torr) at 298 K. The yield of propylene (C_3H_6), the cross-combination product of methyl and vinyl radicals, was compared to the yield of ethane (C_2H_6), the methyl radical combination product. At 27 kPa $[C_3H_6]/[C_2H_6] = 1.28$ was derived. This ratio was reduced to about 0.75 when the pressure was reduced to about 0.28 kPa. Kinetic modeling results indicated that the contribution of the combination reaction $C_2H_3 + CH_3 + M \rightarrow C_3H_6 + M$ to the total cross-radical reactions is reduced from 78% at high pressures (27 kPa) to about 39% at low pressures (0.28 kPa). At low pressures an additional reaction channel, $C_2H_3 + CH_3 \rightarrow C_3H_5 + H$, becomes available, producing a host of allyl radical reaction products including 1,5-hexadiene, the allyl radical combination product. The observed 1,5-hexadiene is strong evidence for allyl radical formation at low pressures, presumably from the decomposition of the chemically activated C_3H_6. Macroscopic and microscopic modeling of product yields and their pressure dependencies were used to interpret the experimental observations. Results of master equation calculations using weak colliders and RRKM theory are in agreement with the observed pressure dependence of the combination reactions. It has been shown that the chemically activated species can undergo unimolecular processes that are competitive with collisional stabilization. The pressure dependence for the unimolecular steps appears as a pressure dependence of the combination/disproportionation ratio. The apparent pathological behavior in this unsaturated system is attributed to the formation of a stronger C−C bond as contrasted to the weaker C−C bond formed from combination of saturated hydrocarbon radicals. This C−C bond strength is sufficiently high for the chemically activated propylene, produced from the methyl and vinyl cross-combination reaction to cleave the allyl C−H bond or isomerize to cyclopropane.

Introduction

Free radicals are critical intermediates in hydrocarbon reaction systems. Termination reactions of hydrocarbon radicals including the absolute and relative rates and products of termination channels are of great importance in understanding and modeling of planetary atmospheric[1−3] and hydrocarbon combustion reactions.[4−6] Relatively little is known about the chemical properties of most hydrocarbon radicals, particularly unsaturated ones.

In recent years, however, there has been limited progress in understanding some aspects of vinyl radical reaction kinetics. Through use of either discharge flow reactor and mass spectrometry[7] or laser photolysis in conjunction with UV kinetic absorption techniques and GC/MS product analysis,[8−10] several kinetic parameters for self-reactions of vinyl radicals and cross-radical reactions of methyl and vinyl radicals have been investigated.[7−10] The kinetic studies of the $C_2H_3 + CH_3$ reactions at 298 K and in the pressure range of 9 kPa (65 Torr) to 27 kPa (200 Torr) established a rate constant of $(1.5 \pm 0.6) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} with the combination reaction producing C_3H_6 being the dominant channel with about 78% yield.[10] No significant pressure effect was observed on the reaction rates and relative product yields in this pressure range.[10] Very recently, Thorn et al.[7b] determined the total rate constant for the vinyl + methyl cross-radical reaction at 0.13 kPa (1 Torr) pressure using a discharge−flow system coupled with mass spectrometric detection. The kinetic studies were performed by monitoring the decay of C_2H_3. The overall rate coefficient at 298 K was determined to be $(1.02 \pm 0.53) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, which is in good agreement with the rate constant value at higher pressures determined in our laboratory, suggesting no significant pressure effect on the total rate coefficient.

Our kinetic measurements of $C_2H_3 + C_2H_3$ combination and disproportionation reactions using excimer laser photolysis with UV−VUV kinetic absorption spectroscopy and GC/MS product analysis established rate constants of 9.5×10^{-11} cm^3 molecule^{-1} s^{-1} for the combination channel yielding 1,3-butadiene, and 3.3×10^{-11} cm^3 molecule^{-1} s^{-1} for the disproportionation

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channel. These studies were performed at 298 K in the pressure range 6.6 to 53 kPa. No variations in the reaction rates and product yields were observed over that pressure range.[8,9] Self-reactions of vinyl radicals have recently been studied by Thorn et al.[7] using the discharge−flow kinetic method followed by direct mass spectrometric detection of vinyl radicals at a nominal pressure of 0.13 kPa. Results of these studies suggest that at very low pressures, the major products of the vinyl self-reactions are ethylene and acetylene instead of 1,3-butadiene.[7a] However, the total rate constant for vinyl self-reactions remains in good agreement with the high-pressure value. Thorn et al.[7a] have suggested that 1,3-butadiene, due to excess internal energy, can isomerize to cyclobutene and then decompose to yield acetylene and ethylene, which are the products of the disproportionation reaction as well. The results of rate constant determinations at very low pressure[7] combined with those at high pressures[8,9] suggest that the contribution to the product distribution from the combination and disproportionation reactions varies significantly with pressure.

The pressure dependence of methyl radical combination has been previously studied experimentally and theoretically.[11−14] Results of these studies indicate a relatively weak pressure effect on the methyl combination reaction. This is consistent with the reverse of the combination reaction being the only energetically open channel; the rate coefficient for this process is small, since the minimum excess energy is zero. Pressure-dependent studies of "falloff" behavior of the rate constant indicate a reduction of rate constant from $(5.0 \pm 0.5) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at high pressures to about 3.5×10^{-11} cm^3 molecule^{-1} s^{-1} at about 0.28 kPa.[12,13]

In this present work we have systematically examined the pressure effect on the combination and disproportionation of methyl−vinyl in the mixed radical system over the pressure range 27−0.28 kPa at ambient temperature.

Approaches

I. Experimental. Experiments were performed using an excimer laser photolysis in conjunction with GC/MS end product analysis. The method has been described in detail previously.[8−10] Briefly, methyl and vinyl radicals were simultaneously produced from the 193 nm photolysis of methyl vinyl ketone ($CH_3COC_2H_3$) in a Suprasil[15] reaction cell. Two self-enclosed gas circulating pumps, one operational to about 40 kPa and another operational at pressures above 30 kPa, were used to flow the gas mixture through the reaction cell so that the cell contents were replaced following each laser pulse. The sample mixture was circulated through a 2 L closed loop. The laser pulse repetition rate was varied between 0.2 and 2 Hz and was chosen so that the sample replacement rate is not exceeded. The active volume of the photolysis cell was 20 cm^3, about 1% of the total sample volume. The photolysis sample consisted of a small amount of the radical precursor ($CH_3COC_2H_3$) in the range 2×10^{15} to 4×10^{15} molecules cm^{-3} in excess amounts of He inert quencher.

The reaction products were analyzed using an on-line Hewlett-Packard 6890 series gas chromatograph.[15] The photolyzed sample was admitted to an evacuated injection loop that was immersed in liquid N_2. The content of the reaction manifold was passed through the loop, and reaction products were collected while the He gas was pumped out. The concentrated sample was warmed to room temperature and directly injected onto two separate capillary columns by admitting the carrier gas into the collection loop. Temperature programming of the oven was required to separate the products. The retention times and response of the gas chromatograph were calibrated by injection of standard samples with concentrations similar to those produced from the laser photolysis. All the reaction products, except methane, could be resolved. The resident time of methane in the GC columns used in this study was very short, and an accurate peak integration was not possible. The sampling manifold for GC was modified, and product analysis of about 1×10^{11} molecules cm^{-3} for hydrocarbons up to C_4 was achieved.

The radical initiator, methyl vinyl ketone, was obtained commercially and was purified by trap-to-trap distillation. The precursor was mixed with ultrahigh purity He (99.9999%), and experiments were conducted at various added He pressures.

II. Theoretical. The macroscopic observables can be related to microscopic (molecular) quantities. The connection of these regimes has been made in chemical activation systems.[16] In the present case the radical combination reactions form highly vibrationally excited molecules in the ground electronic state, which can either be collisionally stabilized via bimolecular collision with other molecules or undergo unimolecular reactions (decomposition or isomerization). For any given system the relative amounts of stabilization (S) and decomposition (D) are pressure- and temperature-dependent. The amounts of S and D depend on the energy distribution ($f(E)$) of the chemically activated reactant, the collision frequency (ω, which is pressure-dependent), and the probability of energy transfer $P(E'-E)$. These factors comprise a generic scheme that enumerates these microscopic competitions and illustrates the deactivation process (stabilization results when $E < E_0$) for a single channel unimolecular reaction:

$\mathrm{R'} + \mathrm{R} \rightarrow \mathrm{R'R(E)}$	$f(E)$
$\mathrm{R'R}(E) \rightarrow$ products (D)	$k(E)$ for $E \geq E_0$
$\mathrm{R'R}(E) + \mathrm{M} \rightarrow \mathrm{R'R}(E') + \mathrm{M}$	$\omega\, P(E',E)/[\mathrm{M}], \quad E > E'$
$\mathrm{R'R}(E') \rightarrow$ products (D)	$k(E')$ for $E' \geq E_0$
$\mathrm{R'R}(E') + \mathrm{M} \rightarrow \mathrm{R'R}(E'')$	$\omega\, P(E'',E')/[\mathrm{M}]$
$\mathrm{R'R}(E'') \rightarrow$ products (D)	$k(E'')$ for $E'' \geq E_0$

For the experiments reported in this paper the helium deactivator (M) must be categorized as a weak collider.[17] The yields of S and D are computed by solving the master equation with the appropriate model for $P(E',E)$[18] and RRKM theory[19] for the $k(E)$'s.[20] If the experiments are in the high-pressure region, then a simple correction to the strong collision model may be used.[21] However, in general, the amount of energy transferred per collision ($\langle \Delta E_{\text{down}} \rangle$ or $\langle \Delta E_{\text{all}} \rangle$ where $\Delta E = E' - E$) must be used. The specific method used for the calculation of S and D can be found elsewhere.[22] Macroscopic observables for two different radical combination systems were calculated: methyl + vinyl and allyl + allyl. Critical energies and the vibrational frequencies for the various reactants and transition states were adjusted to reproduce published Arrhenius parameters; an exponential model with $\langle \Delta E_{\text{down}} \rangle = 400$ cm^{-1} was used to represent the helium deactivator. The details for each system are presented in the next section.

Results and Discussion

The 193 nm photolysis of methyl vinyl ketone ($CH_3COC_2H_3$) was used as the source of methyl and vinyl radicals.[8] Our

TABLE 1: Experimental Conditions and the Measured Ratio of $[C_3H_6]/[C_2H_6]$ at Various Precursor Concentrations and Total Pressures Following the 193 nm Photolysis of $CH_3COC_2H_3$/He Mixtures

$[CH_3COC_2H_3]$ 10^{15} molecule cm^{-3}	[He] kPa (Torr)	$[C_3H_6]/[C_2H_6]$ exptl	$[C_3H_6]/[C_2H_6]$ calcd
3.2	26.6 (200)	1.30	1.38
3.2	16	1.27	
1.6	14.6 (110)	1.26	
3.2	1.76	1.20	
3.2	1.1	0.92	
3.6	0.84	0.87	
1.6	0.81	0.88	
1.6	0.28 (2.1)	0.75	0.75

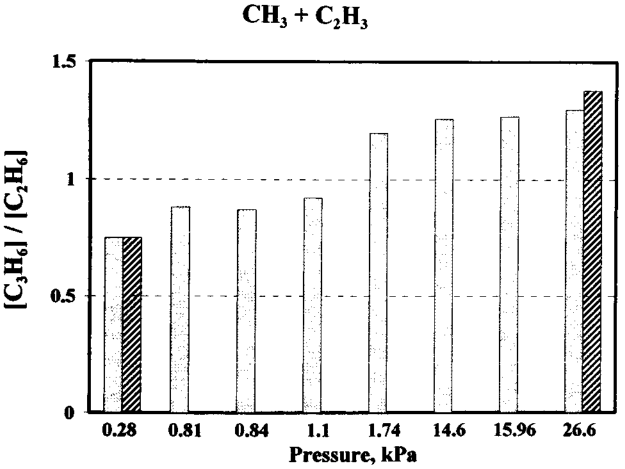

Figure 1. Histogram of $[C_3H_6]/[C_2H_6]$ values for various He pressures determined following the 193 nm photolysis of $CH_3COC_2H_3$/He mixtures (solid bars) and derived from kinetic modeling (dashed bars).

previous studies of this photolytic process indicated nearly identical initial yields of methyl and vinyl radicals.[9,10]

The major reaction sequences following the photolysis can be described as follows:

$$CH_3COC_2H_3 \xrightarrow{h\nu} CH_3 + C_2H_3 + CO \tag{1}$$

$$C_2H_3 + C_2H_3 \xrightarrow{M} C_4H_6 \text{ (1,3-butadiene)} \tag{2c}$$

$$C_2H_3 + C_2H_3 \xrightarrow{M} C_2H_2 + C_2H_4 \tag{2d}$$

$$CH_3 + CH_3 \xrightarrow{M} C_2H_6 \tag{3c}$$

$$C_2H_3 + CH_3 \xrightarrow{M} C_3H_6 \text{ (propylene)} \tag{4c}$$

$$C_2H_3 + CH_3 \xrightarrow{M} C_2H_2 + CH_4 \tag{4d}$$

All the reaction products, except methane, were resolved and quantified using our gas chromatographic analysis method. The yield of propylene (C_3H_6), the cross-combination product of methyl and vinyl radicals, was compared to the yield of ethane, the combination product of methyl radical. A value of $[C_3H_6]/[C_2H_6] = 1.28$ is determined at pressures higher than about 1.7 kPa. This ratio is reduced to about 0.75 at 0.28 kPa. The values of the ratio $[C_3H_6]/[C_2H_6]$ determined experimentally and from kinetic modeling at various pressures are listed in Table 1 and plotted in Figure 1.

The $C_2H_3 + CH_3$ reaction system was modeled at high- and low-pressure conditions using the REACT kinetic modeling program.[15,23] The pressure dependence of the ratio $[C_3H_6]/[C_2H_6]$ depends primarily on the pressure dependence of C_3H_6 formation. The effect of pressure on the methyl radical recombination reaction has been included in the kinetic modeling attempts.

As discussed earlier, our previous studies of $C_2H_3 + C_2H_3$ reactions at high pressures[8,9] and the results of Thorn et al.[7a] at low pressures suggest that the total rate constant for vinyl self-reactions remains unchanged at about 1.28×10^{-10} cm^3 $molecule^{-1}$ s^{-1}. However, the contribution to the product distribution from the combination and disproportionation reactions varies with pressure. In a separate recent study, with only vinyl radicals present, we have determined a value of $[C_4H_6]/[C_2H_4] = 0.6$ at 0.33 kPa and a value of $[C_4H_6]/[C_2H_4] = 3.5$ at pressures above 13.3 kPa.[24] The effect of pressure on the $C_2H_3 + C_2H_3$ reactions was also included in the kinetic simulations of $C_2H_3 + CH_3$ reactions.

The major reaction sequences used in the modeling and rate parameters for the high- and low-pressure conditions are given in Table 2. The initial methyl and vinyl radical concentrations were assumed to be 4×10^{13} molecules cm^{-3}, typical of these experiments. For high-pressure conditions, kinetic modeling yielded a value of $[C_3H_6]/[C_2H_6] = 1.35$, which is in good agreement with the experimental value.

For simulation of the low-pressure conditions the rate constant for methyl self-combination was reduced from 5×10^{-11} cm^3 $molecule^{-1}$ s^{-1} to 3.5×10^{-11} cm^3 $molecule^{-1}$ s^{-1} and the total rate constant for vinyl self-reactions was maintained at $(k_{2c} + k_{2d}) = 1.28 \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}, but the contribution of the combination channel was reduced. By use of a rate constant value of $k_{4c} = 6 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} for

$$C_2H_3 + CH_3 \xrightarrow{M} C_3H_6$$

a value of $[C_3H_6]/[C_2H_6] = 0.75$ was derived from the kinetic simulations. This value is identical to the experimentally determined result.

Figure 1 displays and compares the ratio of $[C_3H_6]/[C_2H_6]$ derived through kinetic modeling with those obtained experimentally at high and low pressures. These results suggest that at very low pressures, the contribution of cross-combination of methyl and vinyl radicals yielding propylene is reduced by about a factor of 2 from its high-pressure value.

One possible mechanism for the reduced yield of propylene (C_3H_6) at very low pressures could be through dissociation of highly excited C_3H_6, that is, $CH_2{=}CHCH_3^* \rightarrow CH_2{=}CHCH_2 + H$. On the basis of the energetics of the reactions involved,[25] such a dissociation is feasible. The cross-combination reaction 4c producing propylene is exothermic by about 423 kJ mol^{-1}, while the dissociation of propylene to allyl radical and an H atom requires about 368 kJ mol^{-1}. In addition, the dissociation of methyl vinyl ketone to produce methyl and vinyl radicals requires 426 kJ mol^{-1}. The absorption of a 193 nm photon (620 kJ mol^{-1}) leaves about 194 kJ mol^{-1} to be distributed among the photofragments. At a helium pressure of 0.27 kPa, the relative number of helium−vinyl collisions is about 1500 times the number of methyl−vinyl collisions. This relative rate coupled with the fact that the average energy removed per collision is greater than 3 kJ mol^{-1} ensures that the vinyl radicals will be thermalized before encountering a photofragment.

The detection of the allyl radical self-reaction and cross-radical reaction products at low pressures provides evidence for the allyl radical presence in the methyl−vinyl mixed radical system. Initially, through kinetic modeling, we estimated the concentration of potential products arising from allyl radical reactions in order to predict if these products would be at a detectable level. Under low-pressure conditions, we assumed

TABLE 2: Primary Reactions and Parameters Used for Modeling of CH_3 and C_2H_3 Mixed Radical Reactions at High and Low Pressures

	rate constant ($\times 10^{11}$ cm^3 molecule^{-1} s^{-1})	
reaction	high P^a	low P^a
$CH_3COC_2H_3 \xrightarrow{h\nu} CH_3 + C_2H_3 + CO$	$[CH_3] = [C_2H_3] = 4 \times 10^{13}$ molecule cm^{-3}	
$C_2H_3 + C_2H_3 \xrightarrow{M} C_4H_6$ (1,3-butadiene)	$k_{2c} = 9.5$	$k_{2c} = 4.5$
$C_2H_3 + C_2H_3 \xrightarrow{M} C_2H_2 + C_2H_4$	$k_{2d} = 3.3$	$k_{2d} = 7.5$
$CH_3 + CH_3 \xrightarrow{M} C_2H_6$	$k_{3c} = 5.0$	$k_3 = 4.0$
$C_2H_3 + CH_3 \xrightarrow{M} C_3H_6$ (propylene)	$k_{4c} = 12$	$k_{4c} =$ adjusted (x)
$C_2H_3 + CH_3 \xrightarrow{M} C_2H_2 + CH_4$	$k_{4d} = 3.3$	$k_{4d} = 3.3$
$C_2H_3 + CH_3 \xrightarrow{M} P$	$k_{4e} = 0$	$k_{4e} = (12 - x)$

[a] Rate constant values as discussed in the text.

TABLE 3: Secondary Reactions and Rate Constants Used, in Addition to Reactions in Table 2, for Numerical Simulation of CH_3 and C_2H_3 Reactions at *Low* Pressures

reaction	rate constant ($\times 10^{11}$ cm^3 molecule^{-1} s^{-1})	ref
$C_2H_3 + CH_3 \xrightarrow{M} C_3H_6$ (propylene)	$k_{4c} = 6.0$	this study
$C_2H_3 + CH_3 \xrightarrow{M} C_3H_5 + H$	$k_{4e} = 6.0$	this study
$C_3H_5 + C_3H_5 \xrightarrow{M} C_6H_{10}$	$k = 3.0$	28
$C_3H_5 + C_3H_5 \xrightarrow{M} C_3H_4 + C_3H_6$	$k = 0.5$	28
$C_3H_5 + CH_3 \xrightarrow{M} C_3H_4 + CH_4$	$k = 0.1$	29
$C_3H_5 + CH_3 \xrightarrow{M} C_4H_8$	$k = 6.4$	30
$C_3H_5 + C_2H_3 \xrightarrow{M}$ products	$k = 8.0$	30, 25
$H + CH_3 \xrightarrow{M} CH_4$	$k = 1.2$	28
$H + C_2H_3 \xrightarrow{M}$ products	$k = 11.0$	32
$H + C_3H_5 \xrightarrow{M}$ products	$k = 28.0$	31

that one-half of the excited propylene dissociates, forming C_3H_5 + H. Then all the major reactions of CH_3, C_2H_3, C_3H_5, and the H atom were included in the reaction mechanism and the final concentrations of the reaction products were evaluated. The initial methyl and vinyl radical concentrations were assumed, as before, to be 4×10^{13} molecules cm^{-3}. Several of the rate constants for allyl radical reactions, particularly at low pressures, are not well-known. Thus, the latest reported values or estimated values were used for the modeling. But for critical rates, such as those for the allyl self-reactions, we used the lower and a higher limit of the rate constant values[28] ($(3.0 \pm 0.5) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}) just to test for the possible range of, for example, the yield of 1,5-hexadiene (allyl combination product). The primary reaction sequences listed in Table 2, at low-pressure conditions, and the secondary reactions and rate parameters listed in Table 3 were used for the modeling of the low-pressure conditions.

Using results of the kinetic modeling, we predicted the yield of the major allyl radical reaction products to be on the order of 2×10^{11} molecules cm^{-3}, which is above the detection limit of our GC/MS analysis methods. The modeling simulations with the inclusion of the secondary reactions resulted in a value of $[C_3H_6]/[C_2H_6] = 0.78$, still in good agreement with the experimentally determined value.

Guided by the modeling results, we did a few careful product analysis experiments at high and low pressures. Initially, the GC retention time and response factor for 1,5-hexadiene were obtained using a known calibration sample of this molecule. Several $C_2H_3COCH_3$/He sample mixtures were photolyzed under identical conditions (laser energy, precursor partial pressure, number of laser pulses) except for the total pressure. The GC analysis of two photolyzed samples, one at high pressure (27 kPa) and one at low pressure (0.3 kPa), indicated the following: (a) the gas chromatogram of the photolyzed sample at low pressure compared to the high pressure is significantly more congested with numerous product peaks that are more pronounced at low pressures; (b) at low pressure (0.3 kPa) there is a considerable amount of 1,5-hexadiene, while at high pressure (27 kPa) only a very small background peak with a retention time of 1,5-hexadiene can be detected; (c) a small peak (2% to 5% of the propylene peak) with a retention time that is the same as that of cyclopropane can be detected at low pressure.

A microscopic representation of the experimental observations and the kinetic modeling is presented as two separate chemical activation systems: one for the methyl + vinyl and the other for allyl + allyl.

The appropriate steps for the methyl + vinyl system are the following:

$$CH_3 + C_2H_3 \rightarrow C_3H_6(E) \qquad f(E)$$

$$C_3H_6(E) + M \rightarrow C_3H_6(E'') + M \qquad \omega\, P(E'',E)/[M]$$

$$C_3H_6(E) \rightarrow CH_3 + C_2H_3 \qquad k'(E)$$

$$C_3H_6(E) \rightarrow C_3H_5 + H \qquad k_1(E)$$

$$C_3H_6(E) \rightarrow \text{cyclo-}C_3H_6(E') \qquad k_{12}(E)$$

$$\text{cyclo-}C_3H_6(E') \rightarrow C_3H_6(E'') \qquad k_{21}(E')$$

$$\text{cyclo-}C_3H_6(E') + M \rightarrow \text{cyclo-}C_3H_6(E'') + M \qquad \omega\, P(E'',E')/[M]$$

The energetics and vibrational frequencies used for the above reactions were those reported earlier.[22] The potential energy profile and the symbols used for the various energies are illustrated in Figure 2.

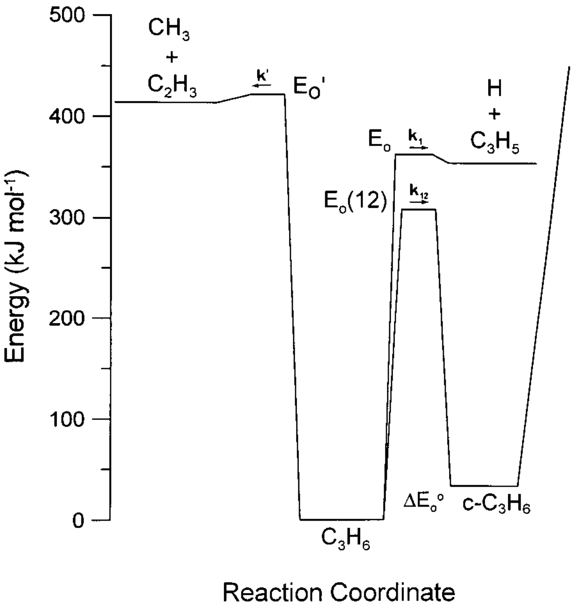

Figure 2. Potential energy profile for the combination of $CH_3 + C_2H_3$ radicals depicting energies of reactants, transition states, and products (propylene, cyclopropane, $H + C_3H_5$).

The $[C_3H_6]/[C_2H_6]$ (which equals k_{4c}/k_{3c} at $p = \infty$) ratio for the weak and strong colliders are shown in Figure 3. The agreement between the RRKM calculations and the experimental results is very good. The decrease in $[C_3H_6]/[C_2H_6]$ with decreasing pressure is more pronounced for the weak collider; the deactivation cascade decreases the probability for stabilization. The system is typical of chemical activation systems with weak colliders. However, the energetics of this system are not typical; normally, the C−C bond energy is smaller than that for a C−H. bond. In the present case the C−C bond adjacent to the π bond is approximately 57 kJ mol^{-1} stronger than the allylic C−H bond. Thus, the chemically activated species has sufficient energy to form C_3H_5 + H.

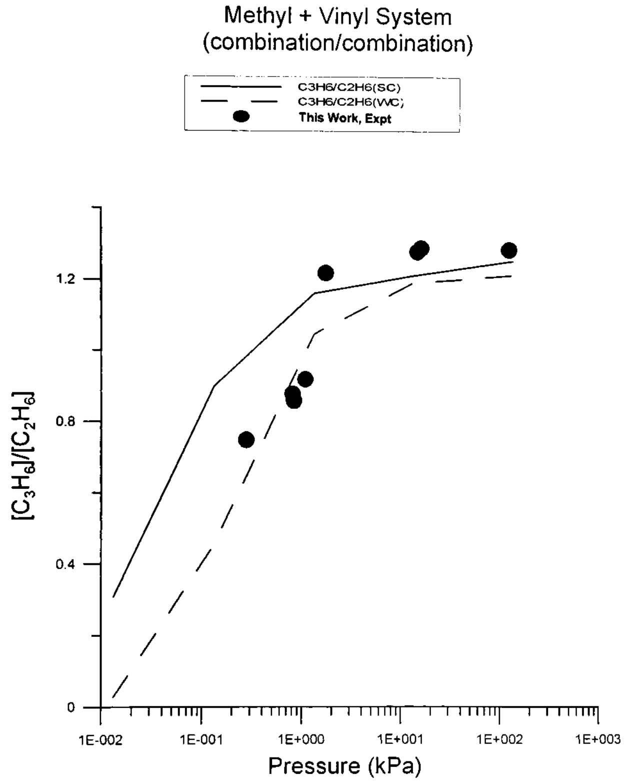

Figure 3. Plots of modeled $[C_3H_6]/[C_2H_6]$ vs pressure for weak collider (dashed line) and strong collider (solid line) at 298 K with experimental points from present work (filled circles).

In addition to the competition between the pressure-dependent stabilization and decomposition (k' and k), the endoergic isomerization of C_3H_6 to cyclopropane must also be considered. At the energies accessible in this experiment this isomerization is faster than the decomposition; at low pressure the isomerization is faster than stabilization. Thus, at low pressure a pseudoequilibrium between propylene and cyclopropane exists. The pressure dependence of $[c\text{-}C_3H_6]/[C_3H_6]$ is illustrated in Figure 4

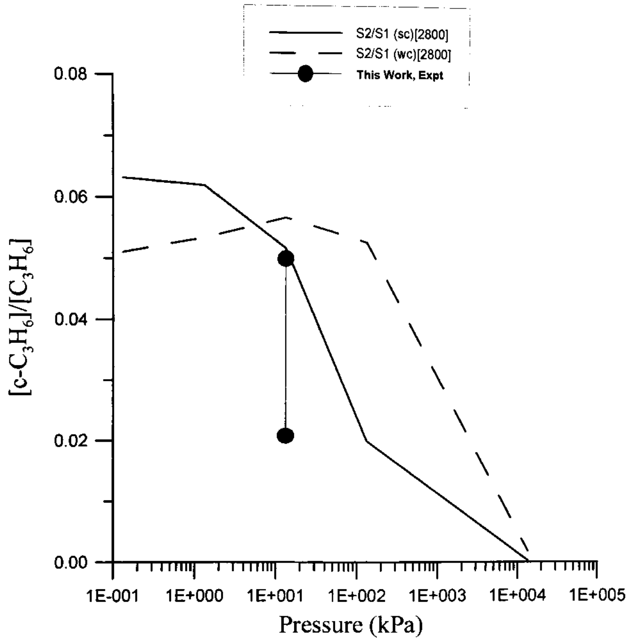

Figure 4. $[c\text{-}C_3H_6]/[C_3H_6]$ vs pressure for weak collider (dashed line) and strong collider (solid line) at 298 K.

for both the strong and weak colliders. At low pressure the ratio is ~0.035; when the pressure is increased so that ω is comparable to k_{12}, then this ratio decreases with increasing pressure. The ratio for the weak collider is smaller than that for the strong collider, since the average energy for the weak collider is less than that for the strong collider and the equilibrium constant ($k_{12}(E)/k_{21}(E)$) decreases with decreasing energy. The experimental results indicate that this ratio is about 3%. Figures 3 and 4 include the strong collider curves for comparison. It can be seen that modeling with a strong collider does not simulate the experimental results. Specifically, this is seen in Figure 4 where the strong collider exhibits a monotonic decrease in c-C_3H_6/C_3H_6 with increasing pressure while the weak collider model shows an increase at low pressure and then a decrease with increasing pressure.

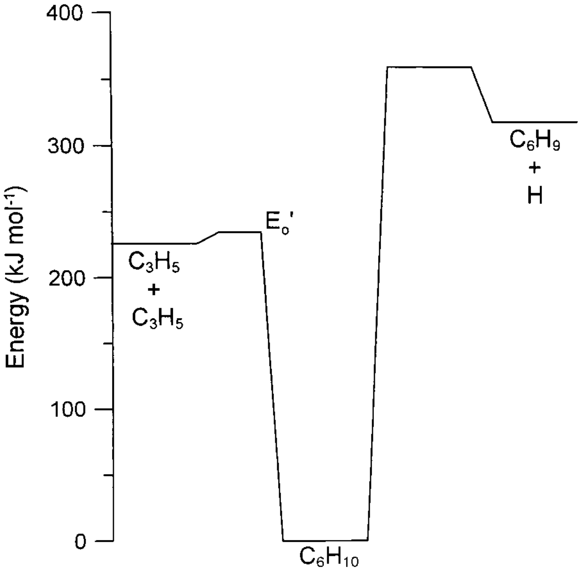

Figure 5. Potential energy profile for the combination of $C_3H_5 + C_3H_5$ radicals depicting energies for reactants, transition state, and products (1,5 hexadiene and H + C_6H_7).

The fate of the 1,5 hexadiene formed by the allyl + allyl combination is also calculated. For this reaction the C−C bond formed is weak, i.e., allylic, so there are no open reactive channels; decomposition corresponding to allylic C−H rupture is ~120 kJ mol^{-1} endoergic. The potential energy profile for these reactions is shown in Figure 5. The microscopic reaction scheme is simple; the only competition is between collisional stabilization and the reverse of the formation reaction:

$$C_3H_5 + C_3H_5 \rightarrow C_6H_{10}(E) \qquad f(E)$$

$$C_6H_{10}(E) + M \rightarrow C_6H_{10}(E'') \qquad P(E'',E)\ \omega/[M]$$

$$C_6H_{10}(E) \rightarrow C_3H_5 + C_3H_5 \qquad k'(E)$$

The vibrational frequencies for 1,5 hexadiene[26] and the transition state were adjusted to give A and E factors that agreed with previously reported values[27] ($\log A/\mathrm{s}^{-1} = 15.3$, and critical energy is 242 kJ mol^{-1}). For a pressure of about 1.3 kPa and at energies typical of this experiment, $D'/S \approx 10^{-5}$, since $k'(E) \approx 10^1\ \mathrm{s}^{-1}$, and for a pressure of 0.4 kPa the collision rate is $10^8\ \mathrm{s}^{-1}$. Thus, the 1,5 hexadiene is quantitatively stabilized.

Conclusion and Summary

An interesting pressure dependence of the cross-radical reactions of vinyl radical with methyl radical was investigated. Macroscopic and microscopic modeling were used to interpret the experimental observations for product yields and their pressure dependences. Kinetic modeling results indicated that the contribution of the $C_2H_3 + CH_3 + M \rightarrow C_3H_6 + M$ reaction to the total cross-radical reactions is reduced from 78% at high pressures (27 kPa) to about 39% at low pressures (0.28 kPa). The chemically activated species can undergo unimolecular processes that are competitive with collisional stabilization. The pressure dependence for the unimolecular steps in the methyl + vinyl system appears as a pressure dependence of the combination/disproportionation ratio. The formation of 1,5-hexadiene at low pressures is strong evidence for the presence of allyl radicals produced from the decomposition of the chemically activated C_3H_6. The apparent pathological behavior in this unsaturated system is attributed to C−C bond formation with greater bond strength as contrasted to a weaker C−C bond formed from the combination of saturated hydrocarbon radicals. The high C−C bond strength is sufficient for the chemically activated proplyene, produced from the methyl and vinyl cross-combination reaction, to break the allyl C−H bond or isomerize to cyclopropane.

Future calculations using ab initio electronic structures will be used to fine-tune the vibrational frequencies and the energetics.

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