The reaction of vinyl radical with alkenes: measured rates and predicted pressure-dependent product distributions.

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Abstract

This work reports experimental and theoretical determination of first-order rate constants for the reaction of vinyl radical with the five smallest alkenes: ethene, propene, 1-butene, 2-butene, and iso-butene. The experiments were performed over a temperature range of 300 K to 700 K at 100 Torr. Vinyl radicals (H_2C=CH) were generated by laser photolysis of vinyl iodide (C_2H_3I) at 266 nm, and time-resolved absorption spectroscopy was used to probe vinyl radicals at 423.2 and 475 nm. The C_4H_7, C_5H_9, and C_6H_{11} potential energy surfaces (PES) for each system were calculated using the G3 method in Gaussian 03. RRKM/ME simulations were performed using VariFlex on a simplified PES for each system to predict pressure dependent rate coefficients and branching fractions for the major channels. A weighted Arrhenius fit to the experimental rate constant at 100 Torr for each alkene is presented. A generic rate rule for vinyl addition to various alkenes is recommended; a similar rate rule for the abstraction of H atoms by vinyl from alkenes is also provided.

Introduction

Reactions involving vinylic radicals are important in combustion processes.[1] The simplest radical of this class is vinyl (C_2H_3), which has a pivotal role in olefin pyrolysis and in the molecular weight growth chemistry associated with soot formation. At high temperatures, vinyl rapidly decomposes to acetylene.[2] In O_2-rich environments, vinyl reacts rapidly to form vinylperoxy, which after several isomerization reactions decomposes to HCO + CH_2O, and thence to CO or CO_2.[4] In O_2-starved environments at lower temperatures, vinyl either will add to unsaturated hydrocarbons, or it will abstract an H-atom; these two competing reactions will create a mixture of dienes, cyclic species, and resonantly stabilized free radicals, each of which can lead to the formation of polycyclic aromatic hydrocarbons (PAH) and other early precursors of soot.[3] Furthermore the addition of a radical species to acetylene, which is present in high concentrations in flames, will yield a vinylic radical. Thus, the relative rates of these addition, abstraction, and oxidation reactions are central in the determination of when various fuels will form soot and when they form complete combustion products. Despite its importance, relatively little experimental work has been performed on vinyl chemistry. This talk presents rate constants for the reaction between the vinyl radical and the first five alkenes

$$C_2H_3 + C_2H_4 \xrightarrow{k_1} \text{products} \qquad (1)$$

$$C_2H_3 + C_3H_6 \xrightarrow{k_2} \text{products} \qquad (2)$$

$$C_2H_3 + 1\text{-}C_4H_8 \xrightarrow{k_3} \text{products} \qquad (3)$$

$$C_2H_3 + 2\text{-}C_4H_8 \xrightarrow{k_4} \text{products} \qquad (4)$$

$$C_2H_3 + \text{iso-}C_4H_8 \xrightarrow{k_5} \text{products} \qquad (5)$$

In the present work, vinyl iodide is used as a clean source to generate vinyl radical. The rate coefficient for the reaction of C_2H_3 with ethene, propene, 1-butene, 2-butene, and iso-butene has been measured over a temperature range of 300 K to 700 K at the pressure of 100 Torr. Detailed quantum calculations have been performed to match the experimental results with theory. The goals of the present work are to establish generic rules for both the addition and H-abstraction reaction rates of vinyl with various alkenes.

Experimental Procedures

The experimental apparatus has been described previously[5], therefore only a brief summary will be given. Vinyl radical (C_2H_3) was generated via laser photolysis of vinyl iodide at 266 nm:

$$C_2H_3I + hv\ (266\ \text{nm}) \rightarrow I + C_2H_3 \qquad (6)$$

Photolysis pulses were generated by frequency-doubling the 532 nm output of a short pulse (2 ns) Nd:YAG laser. Direct absorption by vinyl radical was used to monitor the reaction of vinyl itself and the various olefins. Vinyl radicals were detected by multiple pass laser absorption at one of two absorption lines, 423.2 nm or 472.0 nm. [8-10] The detection wavelength was generated using a mode-locked Ti:Sapphire laser (1.2 ps at 80 MHz) pumped by a 532 nm diode-pumped solid state continuous-wave (CW) laser. The output of the Ti:Sapphire laser was frequency-doubled using a BBO crystal.

The spectral range of the laser, when used with a harmonic generator, covers most of the visible wavelengths allowing for the detection of a wide array of organic radical species. The excellent stability this laser system allows accurate measurement of rate constants from the microsecond-to-millisecond time scale. A Herriott-type multi-pass resonator is used to increase path length up 40 meters. A high resolution spectrometer (0.1 nm FWHM) was used to determine the output wavelength. The spectrum of vinyl radical is ideal for such a probe laser, because its absorption features are broader than the laser FWHM, yet still narrow enough to allow tuning off resonance. The off-resonance signal contains contributions from thermal lensing noise; the vinyl concentration is taken to be proportional to the difference in absorption between traces taken on- and off-resonance.

The experiments were carried out in a 160 cm long temperature-controlled stainless steel flow reactor. To improve the signal-to-noise ratio, a balanced detection scheme was used where a reference beam (I_0) that does not pass through the reactor is normalized to and subtracted from the probe beam (I) using a continuously variable optical attenuator and a low-noise differential amplifier.

To maintain a constant flow of the reactant and buffer gases, calibrated mass flow controllers were used. In most experiments, flow rates were sufficient to completely refresh the cell every 3-5 shots of photolysis laser at 1 Hz repetition. Only ~ 0.2 % of photolyte dissociates on each pulse. The internal pressure of the reactor is measured by a capacitance manometer and controlled via an automated butterfly valve. The flow reactor was housed in a cylindrical oven. Additional resistive heating was supplied to the reactor entrance and exit region. The entrance, center, and exit temperatures were monitored using K-type thermocouples which were fed into three independent PID controllers to maintain a constant temperature.

Vinyl Iodide was purchased from Oakwood Products Inc (C_2H_3I • 90.0%) and was purified by repeated freeze-pump-thaw cycles. Additional gas-phase chemicals were purchased from following suppliers and were used without further purifications: propene • 99.0% (2.0 grade from Advanced Gas Technologies Inc.), 1-butene • 99.0% (2.0 grade from Advanced Gas Technologies Inc.), 2-butene • 99.0% (2.0 grade from Advanced Gas Technologies Inc.) Iso-butene • 99.0% (2.0 grade from Advanced Gas Technologies Inc.), He • 99.999% (5.0 grade, Airgas).

All the experiments were performed between 300 K to 700 K and at a pressure of 100 Torr. To maintain pseudo-first-order conditions, alkene concentrations were in large excess over vinyl concentration. This ensured that the pseudo-first order decays were at least five times faster than the decay without added alkenes. For most of the experiments, vinyl iodide concentrations were maintained at $[C_2H_3I] = 1 \times 10^{15}$ molecules cm^{-3}. Some experiments were performed at several concentrations of vinyl by varying photolysis laser intensity and C_2H_3I concentration. It was found that the rate constants did not depend on $[C_2H_3]$ or on photolysis energy, confirming the validity of a pseudo-first-order approximation and suggesting a negligible role for photolytic interferences. To determine k_{1-5}, the decay rate of C_2H_3 was measured as a function of the alkene concentration. Rate constants were from the slope of a plot of the pseudo-first order rate constant for vinyl loss, k" (where $k" = k_{1-5}\,[C_nH_{2n}] + k_0$), versus $[C_nH_{2n}]$, which yielded a linear slope. The effective rate constant k_0, represented by the zero-alkene intercept of this plot, is attributable to all other loss processes for vinyl radical, including self-reaction, reaction with the photolytic precursor, and diffusion out of the beam. The rate constant for the recombination of vinyl at 298 K was recently determined to be $(6.4 \times 0.7) \times 10^{-11}$ cm^3 $molecules^{-1}$ s^{-1}.[11] The product of this rate constant with the initial concentration of vinyl is within a factor of two agreement with the values for k_0. In contrast, if the rate of vinyl + vinyl-iodide at 298K is approximated by the previously reported[5] rate for vinyl + ethene, or roughly 5×10^{-16} cm^3 $molecules^{-1}$ s^{-1}, then the product of this rate with the initial concentration of vinyl iodide is several orders of magnitude smaller than k_0. Thus, the primary loss channel for the vinyl radical under zero-alkene conditions can be attributed to the vinyl self-reaction. The uncertainty limits of $k\bullet$ represent the statistical uncertainty resulting from the fit of the C_2H_3 decay data to a single exponential. Alkene concentrations used were large enough that the error in simply including the second-order contribution from self-reaction in the intercept was small. Extracting $k\bullet$ from the first-order component of a fit to the functional form for a combined first- and second-order decay resulted in identical values of k_1 to within experimental uncertainty.

Theory

The optimized geometries and zero-point corrected energies for the stationary points, transition states, and product channels on the C_4H_7, C_5H_9, and C_6H_{11} potential energy surfaces were calculated using the G3 compound method[12]; more accurate vibrational frequencies were obtained from subsequent B3PW91/6-311++g(3df,pd) calculations. All quantum calculations were performed using the Gaussian 03 software package.[13] Doublet species wave functions were unrestricted. For each system, a simplified potential energy surface is presented. An RRKM/ME program package, VariFlex[14], was used to calculate the density of states, microcanonical rate constants, and the pressure- and temperature-dependent rate constants for the title reactions. The PES's do not explicitly contain all the possible conformers for a given species; instead, the lowest energy conformer was selected, and other conformers (e.g. cis and trans) were treated as hindered internal rotors. The potential barrier for each hindered rotor, here assumed to be any single carbon-carbon bond not included in a ring, was calculated at the B3PW91/6-31+G(d,p) level. A relaxed scan along the dihedral angle in 10 degree increments was performed, and the resulting potential barrier was fit to a Fourier series. The partition function and density of state for each rotor was treated as a one-dimensional hindered rotor with a semi-classical Pizer-Gwinn[15] –like approximation:

$$Q = \frac{Q_{\text{classical hindered rotor}} Q_{\text{quantum harmonic oscillator}}}{Q_{\text{classical harmonic oscillator}}} \tag{7}$$

Tunneling was included for all transition states by use of an Eckart approximation. For energy transfer in the master equation, a single-exponential down model was used, with an average ΔE_{down} given by 100 cm^{-1} $(T/298)^{0.8}$[16,17]. The collision frequency was estimated using a Lennard-Jones model, with LJ parameters estimated from literature values[18].

Results

To facilitate comparison, the Arrhenius parameters for all five vinyl + alkene systems are summarized in Table 3. Between 300 and 700 K and at 100 Torr, the fastest rate is vinyl + propene, followed by iso-butene, 1-butene, ethene, and 2-butene. Although the experimental rates are quite similar, with less than a factor of five separating the slowest from the fastest, the ordering of the rates cannot be explained solely by molecular weight or reaction enthalpy. Three competing effects determine the relative ranking of the rates: reaction path degeneracy, rotational effects, and the stability of the initial adduct.

Reaction path degeneracy: Statistical factors, such as the external symmetry of the molecule and the number of energetically equivalent transition states, will impact the relative ranking. The external symmetry numbers for the reactants are: vinyl, 1; ethene, 4; propene and 1-butene, 1; 2-butene and iso-butene, 2. The external symmetry number for all the transition states is 1; however, the reactions for propene, 1-butene, and 2-butene each have two energetically equivalent chiral transition states. Thus, the reaction path degeneracy for the reactions are: ethene and 2-butene, 4; propene, 1-butene, and iso-butene, 2. Consequently, other things being equal, one would expect for the reaction of vinyl with ethene or 2-butene to be twice as fast as the other alkenes.

Rotational effects: All of the reactants and transition states may be approximated as oblate near-symmetric tops, with one external moment of inertia significantly larger that the other two. The non-degenerate moments of inertia for ethene and propene are significantly smaller than those of the butenes, as shown in

Table 2. Consequently, due to rotational partition functions only, one would expect the reaction of vinyl + ethene to be the fastest, followed by propene, with the butenes roughly equivalently in third.

Radical stability: The initial adduct for vinyl + ethene is a primary radical; for propene, 1-butene, and 2-butene, the initial adduct of the major channel is a secondary radical; for iso-butene, it is a tertiary radical. Since the reaction barrier should be lower for more stable radicals, from this argument one would expect vinyl + iso-butene to be the fastest and vinyl + ethene to be the slowest. Since the addition of vinyl to an unsubstituted CH_2 end group is less hindered than addition to a substituted carbon, one would expect propene and 1-butene to be faster than 2-butene. Additionally, one would expect 1-butene to be faster than propene due to increased hyperconjugation.

In order to quantify the importance of these competing effects, quantum calculations were performed to calculate the transition-state theory rate constants for all addition and abstraction rates. The importance of radical stability on the barrier height is shown in Table 1. The importance of reaction path degeneracy and rotational effects is shown in

Table 2. A modified Arrhenius fit for both the experimental values and the transition state calculations are shown in Table 3. To determine the temperature exponent for the rate expression, the exponential pre-factor for the transition-state theory rate constant was fit to an equation of the form

$$\frac{k_B T}{h}\frac{Q_{TS}}{Q_{AB}} = A\left(\frac{T}{1000\ [\mathrm{K}]}\right)^{n} \qquad (8)$$

The resulting values for the temperature exponent n are shown in column 3 of Table 3. Between 300 and 700 K, the dominant rate for each vinyl + alkene system is the major addition channel, and the average value of n for these channels is 1.6; thus, to simplify comparison, an average value of n = 1.6 was used for the Arrhenius fits in Table 3.

Rate Rules for vinyl + alkenes: Addition

Based upon the results in Table 1, the following generalizations can be made. If an H-atom is replaced by a CH_3 group on the bonding carbon, the substituted group obstructs the vinyl addition, and the reaction barrier is increased by roughly 0.6 kcal/mol. If an H-atom is replaced by a CH_3 group on the adjacent double-bonded carbon, the resultant radical becomes more stable (e.g. from primary to secondary radical), and the reaction barrier is lowered by roughly 0.6 kcal/mol. In contrast, replacing a CH_3 group with a C_nH_{2n+1} group (for n > 1) will lower the reaction barrier in both cases due to hyperconjugative stabilization. If the substitution is made to the bonding carbon, the reaction barrier will decrease by roughly 0.2 kcal/mol; if the substitution is made to the adjacent double-bonded carbon, the barrier will decrease by roughly 0.5 kcal/mol.

To compare the A-factors, one must take into consideration both the rotational effects and the reaction path degeneracy. Since the rate constants for ethene and propene are disproportionately influenced by their high rotational constants, the A-factors for these two reactions have been omitted from the fitting procedure. Similarly, since the reaction path degeneracy for 2-butene is twice that of the other two butenes, its A-factor will be divided by two. The following generic rule for vinyl + alkenes is proposed:

1. Start with A = 5.8E-14 $*(T/298)^{1.6}$ [cm^3/molecule/s] and $E_{a,0}$ = 3.85 [kcal/mol].
2. Beginning with the bonding atom:
   a. For each methyl group, increase E_0 by 0.8 kcal/mol
   b. For a C_nH_{n+1} group, n>1, increase E_0 by 0.1 kcal/mol
3. For the adjacent double-bonded carbon:
   a. For each methyl group, decrease E_0 by 0.8 kcal/mol
   b. For a C_nH_{n+1} group, n>1, decrease E_0 by 1.2 kcal/mol
4. Multiply the A-factor by the reaction path degeneracy / 2.

A less accurate but more general rule is also provided. This rule assumes that the activation barrier is described by an Evans-Polanyi equation:

$$E_a = E_0 + \alpha \Delta H_0$$

where E_0 and α are empirical constants, and ΔH_0 is the reaction enthalpy at 0K. For this type of rate equation, the following rate rule is recommended:

A = (reaction path degeneracy / 2) × $(8.2)\times 10^{-14}$ cm^{-3} $molecules^{-1}$ s^{-1} $(T/298)^{1.6}$
E_0 = 22.3 kcal/mol
α = 0.59

This rate rule is less accurate than the previously described rate rule. At 300 K, it is off by almost a factor of five; by 700 K, the error is within a factor of two.

Rate Rules for vinyl + alkenes: H-abstraction

As mentioned previously, the vinyl radical can abstract an H-atom from the alkene. For ethene, the result is a symmetric reaction, so it is not considered here. For the other four alkenes, the lowest barrier to abstraction is when the alkene becomes a resonantly stabilized (allylic) radical: propene to allyl, 1-butene and 2-butene to 1-methyl-allyl, and iso-butene to 2-methyl-allyl. Although it is possible for vinyl to abstract other H-atoms, the barriers are significantly higher: for vinyl + propene, the barriers to abstract an H-atom from C1 or C2 are roughly 6 and 4 kcal/mol higher, respectively, and for vinyl + 1-butene, the barrier to abstract an H-atom from the methyl group is 5 kcal/mol higher. The Arrhenius parameters for these calculations are shown in Table 4. Comparing the rates for addition and H-abstraction, it is clear that the addition rates have lower barriers, and that the abstraction rate A-factors have higher temperature-dependencies. Thus, at higher temperatures, the abstraction rates will dominate the addition rate, consistent with entropic intuition.

To generate a rate rule for H-abstraction, it is customary to divide by the number of H-atoms that, when abstracted, will yield identical products. For 1-butene, the H-atom comes from the CH_2 group on carbon C3; for the other three alkenes, the H-atoms belong to methyl groups. Thus, propene is normalized by three, 1-butene by two, and 2-butene and isobutene by six. When normalized in this regard, the rates for abstraction from a methyl group are remarkably consistent, as shown in the last two columns of Table 4. The abstraction rate from propene has a slightly higher A-factor, consistent with the high rotational constant for propene, and it has a slightly higher barrier, consistent with the hyperconjugation of the larger butenes. The rate for abstraction from 1-butene is roughly a factor of five faster between 500 and 2000 K, as expected, since it is easier to form a secondary radical than a primary radical. Based upon the rates presented in Table 4, a generic rule for vinyl H-abstraction is:

For abstraction from CH_3:

1. start with: $A = 1.4E\text{-}14 *(T/298)^{2.5}$ [cm^3/molecule/s] and $E_a = 5.3$ [kcal/mol]
2. multiply by the number of CH_3 groups adjacent to the double-bond.

For abstraction from CH_2:

1. start with: $A = 3.2E\text{-}14 *(T/298)^{2.5}$ [cm^3/molecule/s] and $E_a = 4.4$ [kcal/mol]
2. multiply by the number of CH_2 groups adjacent to the double-bond.

Although the major addition channel is the dominant reaction rate in the experimental temperature range, the H-abstraction channel is not negligible. Indeed, for 1-butene and iso-butene, it can be as much as 25% of the total rate. Consequently, it is important to include both addition and abstraction reactions when comparing the effectiveness of the new rate rule with the experimental data. The rate rules for addition (both major and minor channels for 1-butene and iso-butene) and H-abstraction were applied for the three butenes. At 300 K, the rate rules are off by less than a factor of 2; from 350 K to 700 K, the agreement between the experimental data and the new rate rules is within 50%.

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Tables

	Vinyl addition to unsubstituted center		Vinyl addition to substituted center	
	E_0	ΔH_0	E_0	ΔH_0

Ethene	3.7	-32.5		
Propene	3.1	-32.3	4.4	-30.4
1-butene	2.9	-32.1	3.9	-31.0
c-2-butene			3.9	-32.5
t-2-butene			3.7	-31.2
iso-butene	2.4	-31.9	4.9	-29.9

Table 1: Reaction Barriers and Enthalpies. 0K Reaction barriers (E_0) and enthalpies (ΔH_0) for vinyl + alkenes (current work) in kcal/mol.

	$\frac{m^\dagger}{m}\frac{\sigma}{\sigma^\dagger}$	$\sqrt{\frac{\Theta_A\Theta_B\Theta_C}{\Theta_A^\dagger\Theta_B^\dagger\Theta_C^\dagger}}$
Ethene	4	22.3
Propene	2	8.4
1-butene	2	3.5
Cis-2-butene, trans-2-butene	4	4.6, 5,5
iso-butene	2	4.4

Table 2: Reaction Path Degeneracy and Rotational Effects. m is the number of energetically equivalent chiral states, σ is the external rotational symmetry number, Θ_A is the rotational constant, and the superscript $\dagger$ denotes the transition state.

			Experiment, n=1.6		TST, n=1.6	
	E_0	n	A	E_a	A	E_a
ethene	3.66	1.23	8.66×10^{-13}	3.19	1.20×10^{-12}	3.32
propene	3.08	1.57	1.32×10^{-12}	3.00	1.20×10^{-12}	3.04
1-butene	2.92	1.75	8.85×10^{-13}	2.92	6.90×10^{-13}	3.05
cis-2-butene	3.87	1.67			1.21×10^{-12}	3.92
trans-2-butene	3.68	1.78			1.26×10^{-12}	3.84
2-butene, 50/50			9.47×10^{-13}	3.57	1.23×10^{-12}	3.88
iso-butene	2.38	1.47	7.97×10^{-13}	2.92	3.86×10^{-13}	2.26
propene, minor	4.28	1.88			4.73×10^{-13}	4.16
1-butene, minor	3.90	2.17			3.72×10^{-13}	4.05
iso-butene, minor	4.89	2.09			2.01×10^{-13}	4.92

Table 3: Modified Arrhenius Parameters for Experimental Data and Theoretical Addition Rates. E_0 is the G3 electronic energy at 0K in units of kcal/mol, n is the fitted temperature dependence of the A-factor of the major addition channel, A has units of cm^3/molecule/s, E_a has units of kcal/mol. 2-butene 50/50 corresponds to a 50% by volume blend of cis-2-butene and trans-2-butene, corresponding to the experimental gases.

			TST Rate, n=2.5		Normalized	
	E_0	n	A	E_a	A	E_a
propene	5.97	2.44	4.33×10^{-14}	5.81	1.44×10^{-14}	5.81
1-butene	4.14	2.65	6.50×10^{-14}	4.40	3.25×10^{-14}	4.40
cis-2-butene	5.15	2.52	8.29×10^{-14}	5.14	1.38×10^{-14}	5.14
trans-2-butene	5.72	2.53	8.35×10^{-14}	5.23	1.39×10^{-14}	5.23
iso-butene	5.44	2.47	8.05×10^{-14}	5.34	1.34×10^{-14}	5.34

Table 4: Modified Arrhenius Parameters for H-Abstraction Rates. E_0 is the G3 electronic energy at 0K in units of kcal/mol, n is the fitted temperature dependence of the A-factor of the major addition channel, A has units of cm^3/molecule/s, E_a has units of kcal/mol. The Normalized rates are the TST rates divided by the number of H-atoms which, upon abstraction, yield identical products.

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