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Reactions and Kinetics of Unsaturated C_2 Hydrocarbon Radicals

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1. Introduction

The chemistry associated with small, unsaturated, aliphatic hydrocarbon radicals has significant intellectual interest as well as direct relevance to a host of combustion processes, catalytic reactions, fundamental organic chemistry, and, in certain cases, planetary and astrochemistry. Unsaturated C_2 hydrocarbon radicals are key precursors to formation of aromatic and polyaromatic molecules in both combustion processes[1] and planetary atmospheric environments.[2] These species undergo reactions that are quite exothermic, and the nature of the reaction paths, product channels, and kinetics becomes complicated as the intermediates themselves can undergo subsequent decomposition, isomerization, or reactions. Accurate reaction rate constants as well as detailed product analysis for radical reactions are required to realistically interpret and model macroscopic hydrocarbon reaction systems and to determine the factors affecting the efficiency of the hydrocarbon growth and abundance of various molecular and radical species. It is somewhat unfortunate that the chemical reactions of such unsaturated hydrocarbon radicals have not been investigated with the thoroughness that has been so characteristic of studies of saturated hydrocarbon radical species such as CH_3, but the situation is in flux. This has been due, in part, to the difficulties in cleanly generating these radicals and directly monitoring their time-dependent absolute concentration as is required for the second-order kinetic studies. During the past 20 years, as a result of significant advances in both ab initio electronic structure theory and new experimental approaches, an appreciable level of understanding of the properties of these species and their

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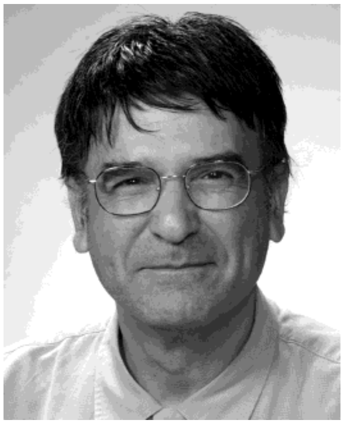
Allan Laufer was born in New York City in 1936. He obtained his B.A. degree in 1956 from the (then) University College of New York University in the Bronx. His Ph.D. was received from Lehigh University in 1962, where he studied the vacuum ultraviolet photochemistry of ethane with James Sturm. Following a short stint in industry, he joined the group of James R. McNesby at the National Bureau of Standards (now the National Institute of Standards and Technology–NIST) in 1964, where he continued studies of vacuum ultraviolet photochemistry. The experimental techniques used naturally led to investigations of the kinetics and spectroscopy of small hydrocarbon free radicals, including that of triplet vinylidene. He joined the Chemical Sciences Division of the Office of Basic Energy Sciences in 1973 as the Program Manager in Chemical Physics and became the Branch Chief for Fundamental Interactions in the Division several years later. Over these years, his research interactions with Askar Fahr continued, and he returned to NIST as a Guest Researcher when he retired from U.S. government service in January 2003.



Askar Fahr received his B.Sc. in chemistry from Ferdowsi University, Mashhad, Iran, in 1975. Subsequently he moved to the United States and attended Georgetown University, where he obtained his M.Sc. (1979) and Ph.D. (1981) in physical chemistry. His Ph.D studies, under the direction of Prof. R. D. Bates, were concerned with kinetics and dynamics of inter- and intramolecular energy-transfer processes. Infrared laser-induced excitation and fluorescence techniques were used. He was a postdoctoral associate (1981–1983) in the Physical Chemistry Laboratory of Oxford University. He has been at the National Institute of Standards and Technology (former NBS) since 1983, where he started his ongoing collaboration with Allan Laufer. He also holds an adjunct professor position at American University, Washington, DC. His research interests include photochemistry, spectroscopy, reaction kinetics, and reaction dynamics of free radicals and transient species pertinent to combustion/soot formation and atmospheric, environmental, and industrial processes.

spectroscopy and electronic structure, as well as their reactions and kinetics, has become available. A number of new experimental approaches make it possible to generate these radicals relatively cleanly and monitor them directly, and attempts are being made to analyze complex reaction kinetic data through detailed kinetic modeling procedures.

As might be predicted for any vibrant research area, reviews of particular aspects of these systems have been published.[3] There has not been a recent comprehensive review dealing with the kinetics of small unsaturated hydrocarbon radicals. In the discussion that follows, we will emphasize the reaction kinetics and mechanisms of product formation of C_2 unsaturated hydrocarbon radicals. The C_2 radical systems discussed will include ethynyl (C_2H), vinylidene ($H_2C{=}C$), and vinyl (C_2H_3) radicals. In the specific area of rate constant determinations, it has been only relatively recently that convenient sources and diagnostics of the reactive radical species have become available. There will be brief discussions of the thermochemistry and both the production and detection of these radical species. While the spectroscopy of these systems is of direct importance, it will be discussed only briefly here, particularly as reviews of some of the earlier work in this area have appeared.[3] In addition, results of the relevant computational studies will be briefly discussed, and preferred rate coefficients for the radical reactions discussed here will be presented.

2. Thermochemistry

To understand the reactivity and kinetics of C_2 radicals, it is important to have firm and consistent values for the thermochemistry of these species. An assessment of the C−H bond energies (DH) of the hydrocarbons, $DH_{298}(\mathrm{HCC{-}H})$, $DH_{298}(\mathrm{CH_2CH{-}H})$, and $DH_{298}(\mathrm{CH_2C{-}H})$, as well as the absolute heats of formation, $\Delta_f H_{298}(\mathrm{HCC})$, $\Delta_f H_{298}(\mathrm{CH_2CH})$, and $\Delta_f H_{298}(\mathrm{H_2CC})$, is a difficult task because of the extreme reactivity of these unsaturated radicals.

Ethylene, $CH_2{=}CH_2$, and acetylene, $HC{\equiv}CH$, are two of the most fundamental unsaturated hydrocarbons. Fragmentation of acetylene produces the ethynl radical, $HC{\equiv}CH\ (X\ ^1\Sigma_g^+) \rightarrow HC{\equiv}C\ (X\ ^2\Sigma^+) + H\ (^2S)$. Likewise, dissociation of ethylene generates the vinyl radical, $CH_2{=}CH_2\ (\tilde{X}\ ^1A_g) \rightarrow CH_2{=}CH\ (\tilde{X}\ ^2A') + H\ (^2S)$. In 1990, negative-ion mass spectrometry and photoelectron spectroscopy were used to determine the bond energies of both ethylene and acetylene.[4] A flowing afterglow device was used to measure the enthalpy of deprotonation of the target species, $\Delta_{\mathrm{acid}}H_{298}(\mathrm{HCC{-}H})$ and $\Delta_{\mathrm{acid}}H_{298}(\mathrm{CH_2CH{-}H})$. In separate experiments, the electron affinities (EA) of the ethynyl and vinyl radicals were measured, $EA(\mathrm{HCC})$ and $EA(\mathrm{CH_2CH})$. The bond dissociation enthalpies were extracted from these data by use of the thermodynamic cycles:[5]

$$\Delta_{\mathrm{acid}}H_{298}(\mathrm{HCC{-}H}) = DH_{298}(\mathrm{HCC{-}H}) + IE(\mathrm{H}) - EA(\mathrm{HCC}) + \int \mathrm{d}T\,[\mathrm{C_p(HCC)} - \mathrm{C_p(HCC^-)} + \mathrm{C_p(H)} - \mathrm{C_p(H^+)}]$$

$$\Delta_{\mathrm{acid}}H_{298}(\mathrm{CH_2CH{-}H}) = DH_{298}(\mathrm{CH_2CH{-}H}) + IE(\mathrm{H}) - EA(\mathrm{CH_2CH}) + \int \mathrm{d}T\,[\mathrm{C_p(CH_2CH)} - \mathrm{C_p(CH_2CH^-)} + \mathrm{C_p(H)} - \mathrm{C_p(H^+)}]$$

Recently, Ervin and DeTuri[6] have reviewed many of the recent bond energy determinations of ethylene and acetylene. High-resolution photofragment translational spectroscopy[7] yields a value for $D_0(\mathrm{HCC{-}H}) = 46\,074 \pm 8$ cm^{-1} or 131.73 ± 0.02 kcal mol^{-1}. The derived bond energy of ethylene, $D_0(\mathrm{CH_2CH{-}H}) = 109.2 \pm 0.6$ kcal mol^{-1}, results from the negative-ion/acidity cycle[4] and is based upon the revised acidity of ammonia. With the established heats of formation[8] of $\Delta_f H_0(\mathrm{CH_2CH_2}) = 12.5 \pm 0.1$ kcal mol^{-1} and $\Delta_f H_0(\mathrm{HCCH}) = 54.3 \pm 0.2$ kcal mol^{-1}, the heats of formation of the radicals can be ascertained, $\Delta_f H_0(\mathrm{CH_2CH}) = 72.1 \pm 0.7$ kcal mol^{-1} and $\Delta_f H_0(\mathrm{HCC}) = 134.6 \pm 0.2$ kcal mol^{-1}. The corresponding room-temperature values are $DH_{298}(\mathrm{CH_2CH{-}H}) = 110.7 \pm 0.6$ kcal mol^{-1} and $\Delta_f H_{298}(\mathrm{CH_2CH}) = 71.1 \pm 0.6$ kcal mol^{-1}; $DH_{298}(\mathrm{HCC{-}H}) = 133.3 \pm 0.3$ kcal mol^{-1} and $\Delta_f H_{298}(\mathrm{HCC}) = 135.6 \pm 0.2$ kcal mol^{-1}.

Thermochemical properties of vinylidene can be extracted from the acidity[4] of the vinyl radical, $\Delta_{\mathrm{acid}} H_{298}(\mathrm{CH_2CH}) = 329 \pm 4$ kcal mol^{-1}, while photoelectron spectroscopy[9] of the $\mathrm{CH_2C^-}$ ion provides the value $EA(\mathrm{H_2C{=}C}) = 0.490 \pm 0.006$ eV (11.3 ± 0.8 kcal mol^{-1}). The ground state of vinylidene is $\mathrm{H_2C{=}C}$ ($\tilde{X}\ {}^1A_1$). These results imply that $D_0(\mathrm{CH_2C{-}H}) = 81 \pm 4$ kcal mol^{-1} and $\Delta_f H_0(\mathrm{H_2C{=}C}) = 102 \pm 4$ kcal mol^{-1}; $DH_{298}(\mathrm{CH_2C{-}H}) = 83 \pm 4$ kcal mol^{-1} and $\Delta_f H_{298}(\mathrm{H_2CC}) = 102 \pm 4$ kcal mol^{-1}. Because the heats of formation of both $\mathrm{HC{\equiv}CH}$ and $\mathrm{H_2C{=}C}$ are known, the energy required for the isomerization of acetylene to vinylidene is fixed[4] at $\Delta_{\mathrm{isomerization}} E_0 = 47 \pm 4$ kcal mol^{-1}.

3. Ethynyl Radical, HC≡C

Early experiments utilized photolysis of bromoacetylene (C_2HBr) as the source of C_2H radicals. But bromoacetylene is probably not the optimum precursor of ethynyl radicals. At wavelengths greater than 160 nm, the photolysis of bromoacetylene has been investigated and is quite complex.[10] Electronically excited Br ($4^2P^0_{1/2}$) formed in the primary process may be quenched, and its subsequent reactions, which will be dependent upon the pressure and nature of the third body, may be one of several possible channels that lead to HBr formation. That, in addition to the explosive nature of C_2HBr, is sufficient motivation for the use of alternative precursors. Most recent results have been garnered using C_2H_2 or CF_3C_2H, photolyzed at 193 nm or shorter wavelengths, as the precursor rather than C_2HBr. Advantages of utilizing the 193-nm photolysis of 3,3,3-trifluoropropyne (CF_3C_2H) are formation of ethynyl radicals with relatively high yields and also the co-formation of CF_3, essentially a benign species that will have less significant effects (compared to H-atoms formed from photolysis of C_2H_2 or halogen (X) atoms from photolysis of C_2HX) on the kinetics and products of C_2H reactions.[11]

The photolysis of acetylene at 193 nm or shorter wavelengths as a photolytic source of ethynyl radicals requires both careful experimentation and interpretation of results. The C_2H generated from this radical source has been shown to have enhanced reactivity due to mixing of the vibrationally excited ground X state formed in the photolysis with the lowest-lying electronically excited A state.[12] The $A\,{}^2\Pi{-}X\,{}^2\Sigma^+$ transition lies in the infrared region, and the extensive vibronic interactions among these two states have complicated the C_2H assignments. Spectroscopic studies of this radical in the IR have reported a large number of bands that have been assigned as transitions to mixed vibronic levels of the ground and first electronically excited states.[13] Wodtke and Lee, using time of flight methods, have determined that up to 16 kcal/mol of translational energy remains in the C_2H fragments. Some of this excess energy may reside in enhanced vibration of the ethynyl radicals,[14] and the role of vibrational excitation in the subsequent chemistry is not clear. An additional complication in the 193-nm photolysis of acetylene is the formation of triplet vinylidene ($\mathrm{H_2C{=}C}$), which has been observed as a major primary process in the vacuum ultraviolet (VUV) photolysis of acetylene.[15]

Difficulties in obtaining accurate rate constants for reactions of C_2H may have been caused, in part, by the absence of an identifiable absorption in the visible and ultraviolet regions of the spectrum, although significant efforts, albeit unsuccessful, have been made in that direction.[10,16] Only very recently, however, Fahr[17] reported the detection of a broad absorption, between 235 and 260 nm, attributed to C_2H with a maximum cross section of $(7.5 \pm 0.9) \times 10^{-19}$ cm^2 molecule^{-1} at 243.5 nm. The spectra obtained from the 193-nm photolysis of both C_2HCF_3 and C_2H_2 radical precursors were nearly identical. The UV absorption feature was assigned to the transitions from the ground electronic state ($X\,{}^2\Sigma^+$) and also possibly from coupled ground and lowest electronic ($A\,{}^2\Pi$) states to the electronic B (or $3\,{}^2A'$) state.[17] Interestingly, the observation of CH ($A\,{}^2\Pi{-}X\,{}^2\Sigma$) chemiluminescence from the reaction of C_2H with O_2 provides another detection technique that allows for indirect monitoring of the C_2H time-resolved concentration.[16]

$$C_2H + O_2 \rightarrow CH(A\,{}^2\Delta) + CO_2 \qquad (1)$$

The technique has now been proven through its use by many investigators. In addition, Stephens et al.[18] have used an infrared absorption at 3593.684 cm^{-1}, a transition originating from the ground vibronic state and a portion of the overall $A{-}X$ transition, to directly monitor the concentration of C_2H. This analysis technique is sensitive to excess vibrational energy in the C_2H, and, as noted earlier, the C_2H radicals formed from the photolysis of C_2H_2 do have significant excess vibrational energy. However, it has been shown that total relaxation occurs, under the usual experimental conditions with sufficient added He as an inert quencher, in about 1 μs.[18]

Relative rate constants for the H-atom abstraction by C_2H from several alkanes and cycloalkanes were reported initially in 1965,[19] and with several alkenes in 1966.[20] The values of the abstraction from the series of alkanes and cycloalkanes were measured relative to

$$C_2H + BrC_2H \rightarrow C_4H_2 + Br \qquad (2)$$

in what is now considered a classic low-intensity photolysis-type experiment using the Hg-resonance line at 253.7 nm as a light source and evaluation of the rate constant ratio, k_2/k_{2a}, from product formation. The study involving alkenes utilized a similar approach.

$$C_2H + RH \rightarrow C_2H_2 + R \tag{2a}$$

In a similar low-intensity photolysis experiment, Cullis et al.[21] obtained a series of relative values for alkanes and several alkynes. Here again, the source of C_2H was the photolysis of bromoacetylene but in the presence of NO. Though NO was recognized as a scavenger of the ethynyl radical, the formation of C_4H_2 was shown to arise from reaction with the radical precursor (eq 2) rather than through the radical combination process,

$$C_2H + C_2H \rightarrow C_4H_2 \tag{3}$$

Bromoacetylene was also used as a precursor to C_2H formation in a microwave flow discharge, followed by mass spectrometric analysis of the reactant and product concentrations.[22]

3.1. $C_2H + H_2$

Measurements of the rate constant of the apparently simple reaction of C_2H with H_2 (eq 4) have generated significant controversy and, with that, improved understanding. Early studies of reaction 4

$$C_2H + H_2 \rightarrow C_2H_2 + H \tag{4}$$

used a microwave flow discharge of bromoacetylene to generate C_2H radicals.[22] H_2 was spatially added, and the measurement of the rate constant for reaction 4, k_4, was obtained by a determination of the temporal profile of the ethynyl under relatively low pressure conditions extant in the flow discharge. The value, $k_4 = 1.7 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}, determined from this study, was the first such rate constant measurement and presaged a relatively intense interest in C_2H reactions, leading to a series of experiments by several groups. The above rate value was considered to be a lower limit, as the authors noted that mixing in the reaction chamber was incomplete.

Other historically early determinations of the rate constant of this reaction were obtained through comparison with reaction 5 and the determination of the ratio of k_4/k_5. The rate constant for reaction 5,

$$C_2H + C_2H_2 \rightarrow C_4H_2 + H \tag{5}$$

as will be discussed later, was obtained through the time-resolved absorption detection of C_4H_2 product as monitored in the vacuum ultraviolet, and a value $k_5 = (3.1 \pm 0.3) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} was derived.[25] With the measured ratio of $k_4/k_5 = 4.9 \times 10^{-3}$, a value of $k_4 = (1.5 \pm 0.2) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} was obtained at room temperature. In subsequent work by Stephens et al.,[18] the rate of appearance of products rather than disappearance of reactants was followed, and, as noted in that work, "there is never a necessity for the rate of appearance of product to be as fast as the rate of disappearance of reactants because the overall reaction can always involve an undetected intermediate" or the presence of side reactions. In yet another experimental approach, Koshi et al.[26] used Lyman-α resonance fluorescence at 121.6 nm of product H-atoms to obtain a rate constant for reaction of ethynyl with H_2, as well as mass spectrometric detection of C_4H_2 product (reaction 5), from which a ratio of $k_4/k_5 = (3.4 \pm 0.2) \times 10^{-3}$ at 298 K could be obtained.[27] The ratio increases significantly with the temperature and reaches $(9.5 \pm 0.2) \times 10^{-3}$ at 438 K. Koshi et al.[26] note that the production rate of C_4H_2 and H-atoms results in the same value for the rate constant; therefore, the formation of an unseen intermediate is considered unlikely in this study. Using the most recent value for k_5 and the ratio of $k_4/k_5 = 4.9 \times 10^{-3}$ determined in a previous work[25] results in a value of $k_4 = 6.4 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}, which is in agreement with an averaged value of most recent reported room-temperature data[18,23,26-30] of $k_4 = 5.4 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}.

By comparison, there are relatively few measurements of k_4 over an extended temperature range where the ethynyl radical is monitored directly. High-temperature measurements are important in the mechanism of acetylene pyrolysis and, more generally, in consideration of an overall hydrocarbon combustion mechanism. Low-temperature measurements are necessary for describing atmospheres extant in the solar system where, for example, C_2H is thought to be an active intermediate, particularly in the carbon-rich atmospheres of the Jovian group such as on Titan, a moon of Jupiter whose atmospheric temperatures range from 95 to 160 K.[24]

A number of studies have examined the temperature dependence of reaction 4 over quite a wide range of temperature, from 180 to 4000 K. Temperature effects raise the issue of an activation energy and the possible role of tunneling, particularly at low temperatures, when H-atom transfer is involved. The reaction has been studied theoretically by Harding et al.,[31] who included a Wigner tunneling correction and obtained an activation energy barrier of 4.0 kcal/mol at the POL-CI level. Herbst[32] calculated the rate coefficient between 10 and 300 K and noted that the tunneling contribution to the overall rate constant becomes dominant at the low temperatures relevant to planetary and interstellar media. More recently, Peeters et al.[30] have performed ab initio calculations up to the coupled cluster level, including all single and double excitations plus perturbative corrections for the triplets, and obtained an adiabatic barrier for H abstraction of 3.1 kcal/mol.

The rate constant of reaction 4 has been determined experimentally over a temperature range from about 180 K through about 4000 K,[23,28,29,33] and the data have been fit[30] to a modified Arrhenius expression over the range from 295 to 700 K:

$$k_4 = (3.92 \times 10^{-19})T^{2.57\pm0.30} \times \exp[-(130 \pm 140)\mathrm{K}/T]\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}} \tag{I}$$

This expression extrapolates remarkably well from the low-temperature data at 220 K[28] upward to the highest temperature of 2000 K.[32]

The rate constant for the reaction of $C_2H + D_2$, k_{4D}, has also been measured. Koshi et al.[27] obtained the ratio of $k_{4D}/k_5 = (0.92 \pm 0.03) \times 10^{-3}$ at 298 K, increasing to $(4.2 \pm 0.5) \times 10^{-3}$ at 438 K. The ratio of the isotope effect decreases from $k_{4D}/k_{4H} = 3.9$ at 298 K to 2.3 at 438 K, while Lander et al.[34] determined the ratio to be equal to 1.9. The kinetic isotope effect has significant theoretical importance, as it is a sensitive test of the shape of the potential energy surface for the reaction, the barrier width, and vibrational factors near the potential minimum. In addition, the large isotope effect confirms the importance of tunneling in “simple” hydrogen abstraction reactions.

An excellent and complete overview of experimental and theoretical work on this reaction, including objective comments on the perceived weakness of some early results, has been published.[23] On the basis of the more recent direct and/or relative rate measurements for reaction 4, we suggest a rate coefficient of $k_4 = (6 \pm 1) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K and an Arrhenius rate expression as given by eq (I) which can be applied over a wide range of temperatures from about 220 to 2000 K.

3.2. $C_2H + C_2H_2$

The extensive use of C_2H_2 as the photolytic precursor of the ethynyl radicals necessitated determination of the rate constant for reaction 5. Cullis et al.[21] report a room-temperature value for k_5 of the order of 10^{-15} cm^3 molecule^{-1} s^{-1}, while Lange and Wagner[22] suggest a lower limit close to 5×10^{-11} cm^3 molecule^{-1} s^{-1} at 320 K. As noted earlier, Laufer and Bass,[25] using the vacuum ultraviolet photochemistry of C_2H_2, obtained $k_5 = (3.1 \pm 0.3) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at room temperature by monitoring the appearance of product C_4H_2 through its absorption in the vacuum ultraviolet. There are, however, a host of more recent data for this reaction[18,26−29,35−40] that agree with a value of $k_5 = 1.3 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at room temperature.

To resolve the rate constant discrepancy for reaction 5, Stephens et al.[18] proposed the formation of an intermediate, C_4H_3, that would have a reasonably long lifetime and dissociate to product C_4H_2 over time. Since Laufer and Bass[25] observed the formation of only the diacetylene product, this would account for the lower limit of the k_5 rate constant. Shin and Michael,[35] however, noted that a measurement involving the formation of H-atoms as a probe yields a rate constant that is in excellent agreement with those obtained by monitoring the disappearance of the C_2H reactant. They suggested, instead, that the proposed short-lived intermediate is vibrationally excited C_4H_3*. The transient intermediate, with a lifetime of about 10^{-11} s to dissociation to vibrationally excited $C_4H_2 + H$, is formed via a barrierless addition process followed by the dissociation. The formation of an excited C_4H_3* had been previously proposed by Homann et al.,[36] who considered possible deactivation to be insignificant under the experimental conditions of their particular experiment and that loss of an H-atom was most probable. In addition, no reaction products of C_4H_3 had ever been detected. Interestingly, the value of k_5 obtained by Homann et al.[36] at 600 K was 3.7×10^{-11} cm^3 molecule^{-1} s^{-1}, in agreement with the values published earlier. There is, at best, a minimal temperature dependence for reaction 5 at temperatures from about 300 to 1475 K.[35] At reduced temperature there is a significant negative temperature dependence[35] that accelerates with decreasing temperatures which reinforces the mechanism of initial formation of excited C_4H_3* without a barrier. Discrepancies between the results of various studies of the $C_2H + C_2H_2$ reaction are an indication of the inherent complexities associated with studies of unsaturated hydrocarbon radicals with low-lying electronic states and reactions which are highly exothermic. Additional care under clearly specified physical and chemical conditions is required in the rate constant measurement.

The presence of complex hydrocarbon molecules in interstellar and circumstellar clouds is well recognized, but the production mechanisms for these carbon-rich entities are not apparent. Reaction 5 is often considered prototypical of the class, especially with a negative temperature coefficient that would result in a rapid rate at the low temperatures typical of the interstellar medium. An ab initio model shows a surface with no entrance potential barrier but with a small exit barrier to products, but at energies less than that of the reactants.[42] There have been two recent joint experimental/theoretical investigations of this reaction. One, a joint molecular beam experiment coupled with a theoretical approach,[43] confirms the mechanism that the C_2H reacts with C_2H_2 to form a C_4H_3 intermediate that can undergo either a low-barrier cis/trans isomerization or a high-barrier 1,2-hydrogen shift. The barrier for the 1,2-hydrogen shift, although high, is still significantly below the total available energy in the system. The occurrence of the latter process is supported by the observation of a minor reaction channel that produces the butadiynyl radical (HCCCC) and H_2. The dominant path, however, is the loss of an H-atom from the intermediate parallel to the angular momentum vector formed in the cis/trans isomerization. A more recent study[44] has obtained a value of $k_5 = (1.3 \pm 0.1) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, which agrees with the other work noted above and provides a similar potential energy surface, i.e., the initial addition is barrier-free, followed by an isomerization prior to dissociation.

3.3. $C_2H + O_2$

The reaction of C_2H with O_2 has been extensively studied due to its importance in combustion reactions. Renlund et al.[16] used the reaction of $C_2H + O_2$ to form CH($A\ ^2\Delta$) (reaction 1), the emission from which served as a monitor of C_2H processes. The kinetic parameters in this work were determined at quite low pressures, and it has been subsequently shown that the internal excitation available to the C_2H fragment from the photolysis of C_2H_2 might be sufficient to initially produce the electronically excited C_2H ($A\ ^2\Pi$) state.[13] The observed emission, attributed to CH($A\ ^2\Delta$) product, then might be due to reaction of the electronically or vibrationally excited ground state of ethynyl radicals.[45]

The variety and complexity that may become apparent in presumed simple reactions are endemic to the C_2H-O_2 system. First, there are a profusion of possible exothermic reactions[46] between O_2 and C_2H, many of which have been observed, viz.:

$$C_2H + O_2 \rightarrow CO + HCO, \quad \Delta H = -151 \text{ kcal/mol} \quad (1a)$$
$$\rightarrow 2CO + H, \quad \Delta H = -136 \text{ kcal/mol} \quad (1b)$$
$$\rightarrow CH + CO_2, \quad \Delta H = -89 \text{ kcal/mol} \quad (1c)$$
$$\rightarrow C_2O + OH, \quad \Delta H = -59 \text{ kcal/mol} \quad (1d)$$
$$\rightarrow HCCO + O, \quad \Delta H = -35 \text{ kcal/mol}^{47} \quad (1e)$$

The CH formed in reaction 1c, as mentioned earlier, has been observed in its $A\ ^2\Delta$ state ($E_0 = 2.87$ eV) as a minor channel of reaction 1 but a major channel from the reaction of $O(^3P)$ with C_2H.[53] The CO product formed from reactions 1a and 1b has been observed in its ground state via its absorption in the VUV[48] and also in the electronically excited $a'\ (^3\Sigma^+)$ state.[49] The a' state of CO lies at 158.3 kcal/mol (55 353.91 cm^{-1}) above the ground state,[50] and the reaction that leads to its formation (reaction 1a) is, therefore, slightly endothermic for formation of the excited state and provides support for the role of C_2H-(A) and/or vibrational excitation in the photolytic production of nascent C_2H.[45] Vibrationally excited CO_2 has also been observed via its IR emission,[49] and HCCO product was observed via mass spectroscopy.[22]

Early rate measurements of reaction 1[22,48] have determined $k_1 \approx 5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. These results have been criticized[22] since the employed methods did not allow for complete mixing in the flow system and only the rate of production of cold CO(X) product was measured.[48] Such a detection method would not have been able to observe the role of a long-lived intermediate, if present. The first rate constant measurement obtained by probing the C_2H concentration directly via its IR absorption was that done by Stephens et al.,[18] who obtained a rate constant value of $k_1 = 4.2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. The order of magnitude discrepancy between the two sets of rate determinations motivated Lander et al.[51] to examine the mechanism in more detail with an aim to better understand both the discrepancy and the reaction mechanism. They found “two types” of CO formation: one is the prompt formation of vibrationally excited CO with a rate that is comparable to the C_2H decay and the higher value of k_1, and a second source via an entirely separate mechanistic process of slow production of ground-state CO that presumably involves an unidentified intermediate with a rate that agrees with the low reported value of k_1[48] and is not equivalent to the rate constant of k_1. The slow rise time of cold CO results, then, from a coupling of several mechanisms as well as vibrational relaxation. OH was not detected in the $C_2H + O_2$ system directly, but it was detected by Lander[51] in the presence of O_2 and additional NO_2 in the reaction mix. The result suggested the formation of OH as a result of the H-atoms in reaction 1b and their subsequent reaction with the added NO_2. HCO could not be detected in the $C_2H + O_2$ system, indicating that reaction 1b is the most probable source of CO.

Opansky et al.[52] were aware that the photolysis of C_2H_2 at 193 nm results in ethynyl radicals with excess energy, either in high-lying vibrational levels of the ground state or residing in the A state, or both. It is recognized that a key aspect of any rate constant determination is to have the C_2H electronically and vibrationally cold, and so SF_6 was added to provide quenching, resulting in a rate constant value of $k_1 = (3.3 \pm 0.3) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 300 K, which is in agreement with several recent determinations.[38,40,53,54] Over the entire temperature range of reported measurements from 15 K[40] through 700 K,[54] there is a very small negative activation energy of the order of $150/T$, which offers some support for the reaction proceeding through a peroxy intermediate, $HCCOO^{\ddagger}$, that can continue to form products or dissociate back to reactants. At elevated temperatures, it is presumed that the fraction of the intermediate adduct that proceeds to product is reduced, resulting in a negative activation energy.

While the structure and nature of the intermediate involved in the $C_2H + O_2$ reaction have been proposed, neither the exact nature of this intermediate nor the actual reaction path is known. A theoretical investigation of the potential energy surface has been carried out by Sumathi et al.[55] using both ab initio and density functional approaches, where it was shown that the initial reaction proceeds without a barrier to form the adduct, HCCOO. A large number of subsequent isomerization or dissociation pathways through ring-forming and ring-opening processes lead to product formation. The dominant channels are predicted to form HCO + CO and HCCO + O. The HCO, however, is predicted to have sufficient internal energy to rapidly decompose to H + CO, in agreement with experimental observation.[51,56]

3.4. C_2H Reactions with Inorganics

The reaction of C_2H with NO has been examined by several groups, in part, as the reaction might play a role in air-assisted hydrocarbon combustion.[18,23,34,56] As in the reaction with O_2, the reaction with NO is quite rapid, with a room-temperature rate constant of about 3.6×10^{-11} cm^3 molecule^{-1} s^{-1}, with a minimal pressure dependence over the rather narrow range from 265 Pa to 2.7 kPa (2−20 Torr). Over the temperature range of 295−440 K, an activation energy of $E/R = -287$ kcal/mol was obtained.[23] The mechanistic situation for reaction of C_2H with NO is not terribly different from that with O_2. There are several possible exothermic reaction channels, and vibrationally excited CO, HCO, HNC, and HCN products all have been observed by time-resolved FTIR emission spectroscopy.[56] A theoretical effort, using density functional theory, to calculate the potential energy surface has been published[57] and indicates that the initial adduct formation occurs in a barrierless manner, with the nitrogen of the NO attaching to the C_2H to form HCCNO. HCN and CO, the most energetically favored products, are formed via isomerization of the HCCNO through a four-membered ring structure—essentially an association/fragmentation mechanism.

The single experimental measurement[38] of the reaction of C_2H with H_2O indicated a relatively rapid

Table 1. C_2H Radical Reactions and Preferred Rate Constant Parameters, Based upon Available Reported Studies

reaction	A (or k)[a]	T/K	n	E/R
$C_2H + H_2 \rightarrow C_2H_2 + H$	$(5.6 \pm 1) \times 10^{-13}$	220−2000	2.57 ± 0.30	$-(130 \pm 140)$
$C_2H + C_2H_2 \rightarrow C_4H_2 + H$	$(1.3 \pm 0.1) \times 10^{-10}$	298		
$C_2H + O_2 \rightarrow$ products	$(3.3 \pm 0.3) \times 10^{-11}$	298		
$C_2H + NO \rightarrow$ products	3.6×10^{-11}	298		
$C_2H + CH_4 \rightarrow$ products	$(2.2 \pm 0.3) \times 10^{-12}$	298		
$C_2H + C_2H_4 \rightarrow$ products	$(1.4 \pm 0.4) \times 10^{-10}$	296		
$C_2H + C_2H_6 \rightarrow$ products	$(3.5 \pm 0.3) \times 10^{-11}$	150−360		(2.9 ± 16)[b]
$C_2H + C_3H_6 \rightarrow$ products	$(2.4 \pm 0.6) \times 10^{-10}$	296		
$C_2H + 1\text{-}C_4H_8 \rightarrow$ products	$(2.6 \pm 0.6) \times 10^{-10}$	296		
$C_2H + C_3H_8 \rightarrow$ products	7.9×10^{-11}	298		
$C_2H + i\text{-}C_4H_{10} \rightarrow$ products	9.6×10^{-11}	298		
$C_2H + n\text{-}C_4H_{10} \rightarrow$ products	1.2×10^{-10}	298		
$C_2H + neo\text{-}C_5H_{12} \rightarrow$ products	1.1×10^{-10}	298		
$C_2H + HCCCH_3 \rightarrow$ products	1.8×10^{-10}	298		
$C_2H + H_2CCCH_2 \rightarrow$ products	$(2.0 \pm 0.5) \times 10^{-10}$	296		
	$(3.0 \pm 1) \times 10^{-10}$	10−100		

[a] Rate constants are in units of cm^3 molecule^{-1} s^{-1}, using the modified Arrhenius form $AT^n \exp[-E/RT)]$. [b] The given error is 16 out of T, where T is between 153 and 357 K. As a percentage of T, the error is approximately 5−10%. The error is based upon the slope of the higher and lower temperature data taken independently. When all the data are included, the slope is nearly zero.[28b]

reaction rate over the temperature range from 295 to 451 K. The reported rate constant, $k = (1.9 \pm 0.2) \times 10^{-11} \exp[(-200 \pm 30)/T]$, or 9.7×10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K, was thought to be too fast for a direct abstraction process, and the authors of this work suggested the formation of an addition complex followed by isomerization and then dissociation to products. A subsequent theoretical calculation[58] is in rather significant disagreement with the experimental results. The former suggest a slow rate constant, indicating that the H abstraction dominates; the theoretical, predicted value of the reaction rate constant is 1.3×10^{-15} cm^3 molecule^{-1} s^{-1}, and the authors consider possible errors in the calculation. The large discrepancies between the reported experimental and computational studies warrant additional investigations of this reaction.

3.5. C_2H Reactions with Saturated Hydrocarbon Molecules

Some of the earliest measurements of ethynyl reactivity were those of its room-temperature reactions with the saturated hydrocarbons CH_4 and C_2H_6.[16,21,59] As in other work, Laufer[59] neither observed nor monitored the C_2H radical directly but only measured the formation of the product C_2H_2 through its intense VUV absorption, from which it was determined that

$$C_2H + RH \rightarrow C_2H_2 + R \qquad (6)$$

$k_6(CH_4) = (1.2 \pm 0.2) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} and $k_6(C_2H_6) = (6.5 \pm 0.4) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, with no detectable pressure dependence over the range 2.7−93 kPa (20−700 Torr) of added helium.

Subsequently, Lander et al.[34] re-investigated these reactions by monitoring the IR absorption of the C_2H reactant and arrived at values that were faster by a factor of about 2 in the case of CH_4 and a factor of 5 in the case of C_2H_6. In the latter reaction, a weak pressure dependence was noted, but the rationale for this observation is not clear, as the reaction is presumably a simple abstraction for which a pressure dependence is not anticipated. The factor of 2, it was noted, may simply result from combined experimental errors, as results from the same laboratory disagreed by about 30%, a most interesting observation that offers some evidence of both the difficulties and the almost obsessive care required in performing these experiments. Opansky and Leone,[28] using transient IR absorption spectroscopy, studied the reaction of C_2H with C_2H_6 over the temperature range from 150 to 360 K and found neither a pressure nor a significant temperature dependence for this reaction, but they determined that $k_6(C_2H_6) = (3.5 \pm 0.3) \times 10^{-11} \exp[(2.9 \pm 16)/T]$ cm^3 molecule^{-1} s^{-1} [$(3.5 \pm 0.3) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K], in agreement with Lander's result. Surprisingly however, an abstraction reaction might be expected to exhibit a positive temperature dependence, as the initial abstraction process usually has a barrier. A significant isotope effect typical for abstraction reactions with both deuterated species vis-à-vis the hydrogenated species of about 2.5 for methane[39] vs 2.2 for ethane[59] was observed. There have been no theoretical calculations that could provide some insight into this dichotomy.

Reactions of C_2H with $RH = C_3H_8$, i-C_4H_{10}, n-C_4H_{10}, and neo-C_5H_{12}, over the temperature range from 155 to 360 K, have been examined[60] by monitoring the ethynyl concentration directly. The rate constants, at 298 K, are listed in Table 1. There are no other direct measurements with which these results could be compared, although there are some extant relative values.[19,61] As in other C_2H "abstraction" reactions, these also exhibit a negative temperature dependence, and the question of a mechanism for these processes remains. Hoobler[60] refers to a paper by Sims,[62] who observed similar behavior in reactions of CN with saturated hydrocarbons. To account for the observed temperature trends, the latter proposed the formation of a transient van der Waals complex that permits the reactant to "find" a favorable orientation for abstraction of the H-atom. As before, theoretical input is necessary for a complete understanding of these mechanisms.

3.6. C_2H Reactions with Unsaturated Hydrocarbons

$C_2H + H_2C{=}CHR$. For the reaction of $C_2H + C_2H_4$, a very rapid rate constant which is almost of collisional frequency[34] of $k = 1.3 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} has been determined. Because of the rapid rate, the mechanism is presumed to be that of addition rather than an abstraction of the strong ethylenic H-atom with its attendant activation energy. Chastaing et al.[40] studied the reactions between C_2H and both ethylene and propylene at temperatures as low as 15 K and observed no pressure dependence but a slight negative temperature dependence on the rate that was, in both cases, about 1×10^{-10}–2×10^{-10} cm^3 molecule^{-1} s^{-1}. The rapid reaction rate is in agreement with a mechanism involving addition to the π-orbital system of the alkene. More recently, the rates of C_2H reactions with C_2H_4, C_3H_6, and 1-butene have been obtained at 103 and 296 K.[63] Here again, the reaction rate constants are quite fast, (1.4 ± 0.4), (2.4 ± 0.6), and $(2.6 \pm 0.6) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, respectively, at 296 K and again with a slight negative temperature dependence that reduces the rate constants by about 20% at 296 K as compared to the values at 103 K. These findings again reinforce a mechanism that involves initial formation of a transient addition complex through capture on a long-range attractive potential energy surface[40] followed by rapid H-atom elimination.

$C_2H + H_2C{=}C{=}CH_2$. The reaction between C_2H and allene ($H_2C{=}C{=}CH_2$) has been examined in a number of studies over the temperature range from 298 K through 63 K.[64–66] The techniques used to achieve the desired low temperatures differ in these works, but the measured rate values are very similar. The reported reaction rate constant at 298 K is $(2.0 \pm 0.5) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} and increases by about a factor of 2 at 63 K, again in agreement with an addition/elimination mechanism. Over the range of 10–100 K, a temperature-independent value of $(3 \pm 1) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} has been recommended.[65]

$C_2H + RC{\equiv}CR'$. The reaction of C_2H with acetylene has been discussed above. As noted previously, reactions of ethynyl with unsaturated hydrocarbons are considered as primary candidates for formation of carbon-rich species in interstellar and exo-planetary space. As a result, reactions of C_2H with several alkynes, in addition to acetylene, have also been examined at low temperatures. Early studies of the reactions of C_2H with other unsaturated hydrocarbons showed remarkable prescience when compared to more recent results. Tarr et al.[20] fully anticipated that the mechanism would involve, in part, the abstraction of an allylic hydrogen from a series of propenes, butenes, and pentenes and all the reactions would have similar rates of abstraction, except from propene because its hydrogens are primary and would have stronger bonding to the carbon. In fact, the observation was that the rate increases with the length of the carbon chain. Another portion of the overall reaction is the initial addition of the ethynyl to the double bond followed by dissociation to products. The measured rate constants are all in consonance with rates for reactions with olefins,[64–66] generally very fast and of the order of collision rates.

Values of the rate constant for reaction of C_2H with propyne ($HCCCH_3$) at various temperatures are 1.8×10^{-10} cm^3 molecule^{-1} s^{-1} at 296 K,[65,66] 2.4×10^{-10} cm^3 molecule^{-1} s^{-1} at 155 K,[66] 2.7×10^{-10} cm^3 molecule^{-1} s^{-1} at 103 K,[62] and 2.9×10^{-10} cm^3 molecule^{-1} s^{-1} at 63 K.[65] The reaction mechanism is expected to be similar to that which has been discussed earlier.[43] The most probable reaction paths have been predicted using coupled-cluster and density functional levels of theory.[67] The reaction is very complex, involving, again, a barrierless entrance channel and numerous rearrangements of the initial adduct with the possible formation of seven different C_5H_4 isomeric products, including ethynylallene (HC_2-$CH{=}C{=}CH_2$) which is formed by the most direct path and involves loss of an H-atom. However, this is not the major product (at least in the case of the reaction of C_2D with CH_3CCH); rather it is methyldiacetylene ($CH_3C{=}CC_2D$), which represents 70–90% of the product.[68]

In general, the kinetics of the C_2H reactions, except for a limited number of reactions, are not very well established. Table 1 lists the C_2H reactions discussed here. Our preferred rate parameters are also listed in the table which are based on the current knowledge of these reactions.

4. Vinylidene Radicals, $R_2C{=}C$:

Vinylidenes ($R_2C{=}C$:) have been implicated as intermediates in organic reactions for an extended period of time.[69,70] The singlet hydrogenated vinylidene ($H_2C{=}C$) that has been reported to be formed from the reaction of C_2 with acetone by a 1,1-abstraction does not react further but can rearrange to acetylene in about 10^{-10} s.[71] Vinylidene was also a postulated intermediate in the vacuum ultraviolet photolysis of CH_2CD_2,[72] which led to the formation of both H_2 and D_2 but no HD. The resulting vinylidene radical, either H_2CC or D_2CC, was assumed to rearrange to form acetylene. Laufer in 1980[73] observed a relatively long-lived transient absorption following the vacuum ultraviolet flash photolysis of C_2H_2 and tentatively assigned the observed absorption lines in the 138–157 nm region to an electronically excited triplet $H_2C{=}C$. A similar absorption was observed from the photolysis of ketene (CH_2CO) whose final products would also be C_2H_2, arising from the combination reaction of two CH_2 radicals. The difference in the two spectra was the temporal history of the transient absorption: that from the direct photolysis of acetylene was present at the shortest times and that from the ketene showed an increase with time. The assignment was confirmed through the distribution of isotopic acetylenes, determined mass spectrometrically, formed in a 1:1 mixture of CD_2 and CH_2.[74] An independent mass spectrometric experiment confirmed the existence of a neutral triplet vinylidene moiety with a lifetime in excess of

Table 2. Quenching and Reaction Rates of Vinylidene Radicals and Preferred Rate Coefficients

reaction	A (or k)[a]	T/K	E/R
$D_2CC\ [a\ ^3B_2] + He \rightarrow D_2CC\ [X(^1A_1)] + He$	$(2.0 \pm 0.3) \times 10^{-15}$	298	
$D_2CC\ [a\ ^3B_2] + Ar \rightarrow D_2CC\ [X(^1A_1)] + Ar$	$(6.6 \pm 0.3) \times 10^{-15}$	298	
$D_2CC\ [a\ ^3B_2] + N_2 \rightarrow D_2CC\ [X(^1A_1)] + N_2$	$(8.5 \pm 0.2) \times 10^{-15}$	298	
$D_2CC\ [a\ ^3B_2] + H_2 \rightarrow D_2CC\ [X(^1A_1)] + H_2$	$(33.8 \pm 6.1) \times 10^{-15}$	298	
$D_2CC\ [a\ ^3B_2] + CO \rightarrow D_2CC[X(^1A_1)] + CO$	$(28.0 \pm 8.0) \times 10^{-15}$	298	
$D_2CC\ [a\ ^3B_2] + CH_4 \rightarrow D_2CC[X(^1A_1)] + CH_4$	$(28.0 \pm 8.0) \times 10^{-15}$	298	
$D_2CC + O_2 \rightarrow CO + DCDO$	$(1.0 \pm 0.25) \times 10^{-13}$	298	
$H_2CC\ [a\ ^3B_2] + He \rightarrow H_2CC\ [X(^1A_1)] + He$	$(1.1 \pm 0.3) \times 10^{-14}$	298	
$H_2CC + H_2 \rightarrow C_2H_3 + H$	2.5×10^{-12}		−3150
$H_2CC + CH_4 \rightarrow C_2H_3 + CH_3$	5×10^{-13}		−2750
$H_2CC + C_2H_6 \rightarrow C_2H_3 + C_2H_5$	1.6×10^{-12}		−2300
$H_2CC + C_2H_4 \rightarrow C_2H_3 + C_2H_3$	1.1×10^{-12}		−2450

[a] Rate constants are in units of cm^3 molecule^{-1} s^{-1}, using the modified Arrhenius expression $AT^n \exp[-E/RT)]$.

0.4 μs[75] that has a barrier to isomerization to acetylene on the triplet surface calculated to be about 48 kcal/mol.[76]

There have been a host of theoretical studies on the very fundamental issue of whether vinylidene actually exists as a bound molecule, i.e., does it represent a minimum on a potential energy surface, what is its lifetime, and what is the barrier to isomerization? With respect to the former, calculations have finally agreed that vinylidene does exist,[77] and that would certainly agree with previous spectroscopic results[73] and the photoelectron spectroscopy results of Ervin et al.,[9] who observed the ground $X(^1A_1)$ state as well as the $a(^3B_2)$ and $b(^3A_2)$ states and determined a lower bound to the singlet lifetime of $\tau > 0.027$ ps and an overall lifetime of 0.2 ps. The singlet lifetime has been calculated to be less than 1 ps,[78] with a barrier to isomerization of about 1.5 kcal/mol[79] on the singlet surface.

In addition to the photolysis of ethylene noted above, vinylidene has been suggested as an intermediate in several pyrolysis systems.[80−83] Several of these interpretations have been questioned through a study of induction periods in the pyrolysis of acetylene[84] and on kinetic arguments.[85] The induction period, it was believed, was not associated with a vinylidene whose lifetime was estimated to be 3.5 μs by a Coulomb explosion determination.[86] In the Coulomb explosion, however, the identity of the vinylidene state (whether singlet or triplet) could not be determined. The lifetime, however, is more commensurate with the triplet. Alternatively, a theoretical approach to acetylene oxidation in shock tubes suggested that vinylidene does play a critical primary role in these processes,[87] which is contrary to Benson's view[85] of the irrelevance of vinylidene in C_2H_2 chemistry. Singlet vinylidene also has been invoked as a primary reactant in the high-temperature oxidation of several unsaturated hydrocarbons,[88] and a rate constant for its reaction with O_2 of 1.6×10^{-11} cm^3 molecule^{-1} s^{-1} has been estimated. The reaction products are assumed to be two HCO radicals, which differs from the triplet vinylidene reaction with O_2 (see below). Further, with a singlet lifetime of less than 1 ps, it is difficult to conjure a reaction of the singlet other than quenching, which has a rate constant that is not significantly larger and closer to a collisional value than that reported above.

However, there have been only a few "direct" kinetic measurements involving vinylidene. The lifetime of the singlet is very short before isomerization, and the singlet is unlikely to be involved in chemical reaction. Several measurements involving the triplet excited state have been reported. The first involved the quenching of both protio and deuterio (deuterated) triplets by He and C_2H_2,[89] with values of $k_{H-He} = (1.3 \pm 0.3) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} and $k_{D-He} = (2.4 \pm 0.4) \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} (for the deuterio analogue). The large isotope effect, 5.4, suggests that collisionally induced quenching occurs through a C−H mode. An upper limit to quenching of the hydrogenated species by acetylene has been estimated[89] as $k = 3.5 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}.

Spectroscopic confirmations of the presence of triplet vinylidene subsequent to the vacuum UV photolysis of C_2H_4 and C_2H_2 have been obtained.[90] In the case of acetylene photolysis, the temporal profile of the transient species suggests that vibrationally relaxed triplet H_2CC is a primary product of the photolysis, as noted above. In the photolysis of C_2H_4, however, the relaxed triplet is not a primary product but is instead formed through an indeterminate secondary process. The reaction of H_2CC with the C_2H_4, expressed as the sum of quenching and reaction, has a rate constant of 1.4×10^{-11} cm^3 molecule^{-1} s^{-1}, while that for D_2CC with C_2D_4 is an order of magnitude slower, 1.4×10^{-12} cm^3 molecule^{-1} s^{-1}.

The H_2CC produced from the vacuum ultraviolet photolysis of dilute mixtures of vinyl chloride (C_2H_3Cl)[91] in helium confirmed the above quenching value for He as $(1.07 \pm 0.17) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} and that for quenching by C_2H_3Cl as 3.5×10^{-11} cm^3 molecule^{-1} s^{-1}.

Rates for the collisional quenching of D_2CC ($a\ ^3B_2$) with He, Ar, N_2, H_2, CO, and CH_4 have also been determined using VUV flash photolysis−kinetic absorption spectroscopy.[92] No evidence of any chemical reaction was detected. The reported rate constants for collisional quenching of D_2CC ($a\ ^3B_2$) are listed in Table 2.

The interaction of ground-state triplet O_2, however, with the deuterio vinylidene does lead to a spin-allowed chemical reaction with the formation of CO and DCDO in equal amounts,[93] with a rate constant of $(1.0 \pm 0.25) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. The suggested mechanism is reaction through O_2 addition across the C=C double bond, forming a cyclic four-membered C- and O-atom-containing ring which is then followed by ring-scission.

$$H_2C{=}C + O_2 \rightarrow H_2CO + CO \tag{7}$$

As a product of the vacuum ultraviolet photolysis of both ethylene and acetylene, the reactions of triplet vinylidene with certain hydrocarbons are of interest in modeling efforts to describe the atmospheres of several of the planets of the outer solar system, where the major source of solar radiation is at Lyman-α (121.6 nm). Estimates of rate constants for a series of simple H-abstraction reactions by triplet vinylidene, for which experimental data are still not available, have been obtained using a bond strength−bond length calculation.[94,95] The rate constants are only for abstraction and do not include other pathways that might even lead to the same product. The triplet vinylidene reactions with H_2, CH_4, C_2H_6, and C_2H_4 and corresponding predicted rate constants are listed in Table 2. The calculated results are estimated to have errors in the activation energy of several kcal/mol and an inaccuracy in the pre-exponential term of a factor of 2−3. While these values do not match either an experimental study or more sophisticated theoretical predictions, these rate parameter estimates are included as they may be of use in model estimates in the absence of other information.

5. Vinyl Radical, $H_2C{=}CH$

The vinyl radical, C_2H_3, is one of the simplest open-shell olefinic species. Due to its central role in free radical chemistry and its relevance to both combustion and planetary atmospheric environments, it has been the subject of considerable experimental and theoretical studies. Yet, despite significant efforts, relatively limited information about the spectroscopy and reaction kinetics of vinyl radicals is available. This has been due partly to difficulties involved in the clean generation and sensitive detection of vinyl radicals plus the high reactivity of these radicals. In recent years, however, progress in understanding some aspects of the gas-phase chemistry and spectroscopy of vinyl radicals has been forthcoming.

Absorption due to the vinyl radical has been observed at selected regions over the entire spectrum. Knowledge of the spectroscopic properties of radicals often is essential for direct probing and kinetic studies of these highly reactive transient species. Absorption, in the region of 400−530 nm, via the $A\,^2A'' - X\,^2A'$ electronic transition was identified by Hunziker et al.,[96] and the same electronic transition was also recently detected using cavity ring-down (CRD) spectroscopy.[97] Fahr et al.,[98] using UV−CRD spectroscopy, identified a diffuse absorption band in the spectral range 225−238 nm, which was assigned as the $B-X$ electronic transition. The reported absorption cross sections vary from 9.2×10^{-18} cm^2 molecule^{-1} at 225 nm to $2.1 \times 2 \times 10^{-18}$ cm^{-2} molecule^{-1} at 238 nm.[98] Detection and characterization of two relatively sharp and intense absorption features at 164.4 and 168.3 nm have also been reported by Fahr and Laufer,[99] obtained by using VUV flash photolysis in conjunction with VUV absorption spectroscopy. The infrared spectroscopy of the ground-state vinyl radicals has been reported by Kanamori et al.,[100] obtained by using IR−diode laser absorption measurement in the region of 820−960 cm^{-1}. More recently, the infrared emission spectrum of vibrationally excited vinyl radical was recorded, and its fundamental vibrational frequencies and relative intensities were determined.[101]

5.1. $C_2H_3 + C_2H_3$

The direct determination of rate constants for second-order reactions such as the vinyl radical−radical disproportionation (eq 8) or combination (eq 9) reactions is a difficult measurement, particularly since an accurate determination of the radical concentration is necessary. Alternatively, it might be thought that an evaluation of the ratio k_8/k_9 of the two reactions might be easier, as it "only" requires accurate product analysis in addition to a convenient radical source.

$$C_2H_3 + C_2H_3 \rightarrow C_2H_4 + C_2H_2 \tag{8}$$

$$C_2H_3 + C_2H_3 + M \rightarrow H_2C{=}CHCH{=}CH_2 \text{ (1,3-butadiene)} + M \tag{9}$$

5.1.1. Disproportionation/Combination

The study of vinyl radicals has a long and checkered history. The products expected from both the disproportionation and combination reactions of vinyl radicals were observed in a sodium diffusion flame experiment using C_2H_3I[102] as the vinyl radical source. The experiment, however, did not allow the unequivocal identification of the formation mechanism, although the disproportionation/combination reactions were considered likely. The effort to study vinyl radicals continued with an investigation of the photolysis of $(C_2H_3)_2Hg$,[103] where it was shown that much of the products were generated through a chain decomposition and that the disproportionation/combination reactions were but chain-terminating steps. MacFadden and Currie,[104] using flash photolysis of $(C_2H_3)_2O$ coupled to a time-of-flight mass spectrometer for product analysis, determined a bimolecular rate constant of $(5.3 \pm 0.5) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} from vinyl decay. Butadiene was seen as only a minor product; thus, the vinyl decay rate was thought to be due to the disproportionation channel. Weir[105] produced vinyl radicals through the CH_3-sensitized decomposition of acryaldehyde (CH_2CHCHO), which was followed by the decomposition of the intermediate:

$$CH_3 + CH_2CHCHO \rightarrow CH_4 + CH_2CHCO \tag{10}$$

$$CH_2CHCO \rightarrow CH_2CH + CO \tag{11}$$

The product distribution was determined by gas chromatography, and k_8/k_9 was found to be equal to 1.1 at 450 K at 13 kPa (100 Torr). Szirovicza[106] used a similar technique to produce the vinyl radical, i.e., the radical-sensitized decomposition (with isopropyl radicals) of the acrylaldehyde, but the k_8/k_9 ratio was found to be 0.02 ± 0.01, in significant disagreement with the earlier result.

Inorganic metal-containing vinyl compounds have also been widely used as sources of vinyl radicals. The disproportionation/combination ratio was determined in a study involving tetravinyl tin, $Sn(C_2H_3)_4$, as the radical source.[107] Combination and disproportionation products were formed even in the presence of O_2, which suggests that molecular-type processes were involved in the photolysis, as the O_2 would be a scavenger of the radicals. If the products so formed were indeed from molecular elimination, then the difference between the total yield and that with O_2 present could be attributed to reactions of vinyl radicals. Under these circumstances, a ratio of $k_8/k_9 = 3.70$ was deduced. The VUV flash photolysis of dilute mixtures of $(C_2H_3)_2Hg/He$ has also been used as a radical source. Using gas chromatographic product analysis, a value of $k_8/k_9 = 0.21 \pm 0.03$ was derived at 53 kPa (400 Torr) total pressure (primarily He).[108]

The photolysis of vinyl iodide also yields vinyl radicals.[109] The low-intensity photolysis, done primarily at 253.7 nm, showed that hydrogen abstraction by C_2H_3 can be quite important. Similarly, Yamashita et al. showed that addition of a radical scavenger, NO, to the system essentially quenched the formation of both C_2H_4 and C_4H_6, while the formation of C_2H_2 was only partially affected. The different mechanisms, in part, are probably due to the presence of energetic C_2H_3 radicals formed in the initial dissociation. The dissociation of vinyl into C_2H_2 + H (reaction 12) is endothermic only by about 35

$$C_2H_3^* \rightarrow C_2H_2 + H \qquad (12)$$

kcal/mol;[46] thus, the initial photon energy (112.7 kcal) is more than adequate to initiate the dissociation. The excess of C_2H_2 over C_2H_4 has also been noted in a subsequent study.[107] The disproportionation/combination ratio also had a wavelength dependence: the reaction at higher energy had a value of $k_8/k_9 = 2.5$, while that at 313 nm had a value of 0.4. The dissociation of the intermediate vinyl radical and wavelength dependence of k_8/k_9 suggest the presence of excess vibrational energy in the intermediate vinyl species which could be eliminated by addition of excess inert quenching gas. Takita et al.[110] obtained a value of about 3 for k_8/k_9 in a high-energy system involving the acetylene-photosensitized decomposition of CH_4 at 147 nm, where the vinyl is formed from the reaction of H + C_2H_2. Ibuki et al.[111] also produced vinyl from the reverse of reaction 12, where the H-atom was formed in the Hg6($^3P_1$)-sensitized decomposition of H_2 and where the H_2 was maintained in excess of 80 kPa (600 Torr). A value of $k_8/k_9 = 0.087$ was determined.

The disparity in these earlier results, suggesting $k_8/k_9 = 0.02-3.7$, is significant and beyond the experimental uncertainties of each measurement. As the most recent results indicate and will be discussed here, it is now evident that pressure has a very significant effect on the product channels of radical–radical reactions involving unsaturated systems and the apparent ratio of combination/disproportionation.

In a series of more recent studies, Fahr et al.[112,114] utilized photolysis of methyl vinyl ketone ($CH_3COC_2H_3$) at 193-nm and also 248-nm photolysis of divinyl ketone and vinyl iodide as vinyl radical sources[112a] which are experimentally preferable to divinyl mercury, as the latter is difficult to handle and readily decomposes on many metal surfaces. In comparison, the 193-nm photolysis of methyl vinyl ketone was found to be a clean source of both C_2H_3 and CH_3 with nearly 1:1 yields. Product studies following photolysis of this precursor, at 13.3–53.3 kPa (100–400 Torr) pressures, yielded $k_8/k_9 = 0.31 \pm 0.06$, which is in reasonably good agreement with previous results from the same laboratory but which used VUV photolysis of divinyl mercury as the radical source.[108] Within the pressure range of those later studies, the combination product 1,3-butadiene was the dominant product, and the ratio k_8/k_9 had no detectable pressure dependency.

The vinyl radical self-reaction kinetics and products have also been studied by Thorn et al.,[113] at nominal pressures of about 13.3 Pa (1 Torr), using direct mass spectrometric detection of vinyl radicals as well as the reaction products. Under the conditions of this study only acetylene and ethylene, the disproportionation products, were detected. The combined results of Fahr et al.[112,114] at high pressures and Thorn et al.[113] at very low pressure indicate a very significant pressure effect on product channels affecting variation of the product distribution with pressure and thus the apparent ratio of k_8/k_9. Under the high-pressure conditions (13.3–53.3 kPa), the combination reaction yielding 1,3-butadiene is the dominant process, accounting for about 75% of the vinyl self-reaction. At very low pressures (13 Pa), however, the major products of the vinyl self-reactions are ethylene and acetylene instead of 1,3-butadiene. The combination channel for vinyl radical self-reaction is highly exothermic (about 116 kcal/mol). The observed pressure dependence is proposed to be due to the competition between collisional stabilization, isomerization, and/or decomposition of the combination adduct, $C_4H_6^*$. A low-energy reaction path involving the isomerization of the initially formed 1,3-butadiene to cyclobutene followed by a unimolecular dissociation to C_2H_2 and C_2H_4 has been proposed.[113] In contrast to the combination path, the disproportionation channel distributes its exoergicity to two fragments: the H donor and the H acceptor. In general, there is insufficient energy in these fragments to promote unimolecular processes.

5.1.2. Kinetics of $C_2H_3 + C_2H_3$

The vinyl radical self-reaction kinetics has been studied directly by Fahr et al.[108,112,114] over the pressure range of 6.7–53.3 kPa (50–400 Torr), using different radical precursors and detection/analysis methods. Results of those studies suggest a total rate constant value of $k_8 + k_9 = (1.25 \pm 0.3) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. Under the pressure conditions of those studies, the combination channel producing 1,3-butadiene was identified as the dominant channel, with a rate coefficient of $(0.9 \pm 0.2) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}.[112,114] At the low pressure of 13.3 Pa (1 Torr), Thorn et al.[113] have obtained a total rate constant of $(1.4 \pm 0.6) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} for the vinyl self-reaction which, within the measurement uncertainties, is in good agreement with the rate constant value determined at higher pressures, suggesting no pressure effect on the overall rate constant for vinyl self-reaction. However, as discussed earlier, the combined results from the two laboratories indicated a very significant pressure dependence of the product channels.

Fahr and Laufer[112b] also examined the deuterium isotope effect on the combination and disproportionation channels of the vinyl self-reaction. Hydrogenated or deuterated vinyl and methyl radicals were generated from the 193-nm photolysis of protio or perdeuterated methyl vinyl ketone. On the basis of product yield measurements, no isotope effect was observed for the combination reaction, predictably, since such reaction involves only C−C bond formation. However, an isotope effect of $k_H/k_D = 1.2$ was determined for the disproportionation reaction, similar to that found for saturated hydrocarbon radicals.

The rate constant of the vinyl−vinyl self-reaction is very fast, about one effective reaction in every two collisions. The usual argument[114] is that reaction of spin-doublet species, such as vinyl radicals, can lead to three dissociative triplet states and one bound singlet, and hence an efficiency of one in four collisions. But vinyl radicals are different because of the presence of an energetically accessible bound triplet state of 1,3-butadiene, the $^3B_{1u}$ state 3.2 eV above the ground state.[114] The combination reaction is exothermic by 116 kcal/mol (5.03 eV),[46] and the triplet state is both thermochemically and spin accessible via reaction of two doublets. If the 1,3-butadiene is formed on the excited triplet surface, spin-induced quenching to the ground state is possible. The presence of triplet butadiene has not yet been observed as a product of the vinyl combination reaction.

5.2. Reactions of C_2H_3 with Other Hydrocarbon Radicals

5.2.1. $C_2H_3 + CH_3$

Fahr et al.[112,114] reported the first direct rate measurement and product studies of the $C_2H_3 + CH_3$ reaction, employing excimer laser photolysis for generating the radicals, kinetic absorption spectroscopy for probing the time profile of the reactants and/or products, and GC/MS end-product analysis for identifying and quantifying the final reaction products.

$$C_2H_3 + CH_3 \rightarrow CH_4 + C_2H_2 \qquad (13a)$$

$$\rightarrow C_3H_6 \qquad (13b)$$

With $CH_3COC_2H_3$ as a photolytic source of both methyl and vinyl radicals, an overall rate constant of $k_{13a} + k_{13b} = (1.5 \pm 0.3) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} was determined.[114] Analysis of the photolyzed samples, over a pressure range of 9.3−23.6 kPa, identified formation of propene, acetylene, and methane, with propene being the major product. On the basis of the results of the optical rate measurements and the product yields, rate constants of $k_{13a} = (0.34 \pm 0.07) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} and $k_{13b} = (1.2 \pm 0.3) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} were derived from these studies.

The combination reaction 13b is about 101 kcal/mol[46] exothermic, and the large value for k_{13b} is comparable to that from vinyl−vinyl and possibly results from the presence of an accessible bound low-lying triplet of propylene at 98.0 kcal/mol (4.25 eV).[116] The kinetics of the C_2H_3 and CH_3 cross-radical reaction has been studied in two other laboratories, using different methods for production and/or detection of methyl and vinyl radicals. At the low pressure of 0.13 kPa (1 Torr), Thorn et al.,[118] using a discharge flow system coupled to a mass spectrometer, determined an overall rate constant value of $k_{13} = k_{13a} + k_{13b} = (1.02 \pm 0.53) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} by monitoring the decay of the C_2H_3 under conditions of excess CH_3. Stoliarov et al.[119] employed the 193-nm photolysis of methyl vinyl ketone to generate the radicals and time-resolved photoionization mass spectrometry for probing the radicals and products. The overall rate constant for the reaction $CH_3 + C_2H_3$ was determined at low pressures of 0.12−0.5 kPa (0.9−3.7 Torr) over the temperature range of 300−900 K. The rate constant, k_{13}, was found to be independent of pressure in the narrow pressure range of this study, with a slight negative temperature dependence, represented by the expression $k_{13} = (5.1 \times 10^{-7})T^{-1.26} \exp(-362/T)$ that extrapolates to a rate constant of $k_{13} = (1.15 \pm 0.11) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K. Results of rate measurements for reaction 13, reported from three laboratories, are in good agreement, and a simple average of the rate constant values, $k_{13} = (1.3 \pm 0.3) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K, can be recommended.

As noted above, in general, radical−radical reactions involving C_2H_3 radicals are quite exothermic, and that is manifested either by formation of an electronically excited combination adduct or in a pressure effect on the product distribution. The effect of pressure on the product channels of the $C_2H_3 + CH_3$ reaction has recently been studied in the above-mentioned three laboratories.[116−119] A value of $C_3H_6/C_2H_6 = 1.28$ has been determined at 298 K by Fahr et al.[117] at about 27 kPa (200 Torr), where the C_2H_6 arises from the combination of CH_3 radicals, used as a reference reaction. But this ratio was seen to decrease to 0.75 at about 0.27 kPa (2 Torr).[117] At low-pressure conditions, formation of additional products, not present at higher pressures, was observed. These included 1,5-hexadiene, the product of the combination of allyl (C_3H_5) radicals, and a number of other C_5 and C_6 products. Results of the study offered clear evidence for the occurrence of the unimolecular dissociation (eq 13c).[117]

$$C_3H_6^* \rightarrow C_3H_5 + H \qquad (13c)$$

Rice−Ramsperger−Kassel−Marcus (RRKM) calculations indicated that the major processes for vibrationally excited propylene (reaction 13b) in He at low pressures are stabilization and decomposition via rupture of the allylic C−H bond to form allyl (C_3H_5) radicals.[117] Product studies of reaction 13, reported by Thorn et al.[118] and Stoliarov et al.,[119] at low-pressure conditions also indicated formation of C_3H_6, C_2H_2, and C_3H_5 as products of the combination stabilization, disproportionation, and combination–decomposition channels, respectively. Results obtained by Stoliarov et al.[119] at $T = 900$ K suggest that production of allyl radicals becomes the major channel. The dissociation of propylene formed in reaction 13b to C_3H_5 (allyl) + H atom (reaction 13c) is endothermic by 88 kcal/mol,[46] but the combination reaction 13b is exothermic by about 101 kcal/mol, providing sufficient excitation energy for the dissociation channel (reaction 13c) to occur. The experimentally observed pressure dependence of reaction 13b is a direct manifestation of the pressure dependence of the unimolecular dissociation (reaction 13c). The unimolecular dissociation has been treated through a master equation approach and RRKM theory, which indicates that the C–C bond formed from the $CH_3 + C_2H_3$ association is sufficiently strong to allow the breaking of a C–H bond, to form allyl or, alternatively, isomerize to cyclopropane.[117] Isomerization to cyclopropane is fast but is a minor process. Alternate third bodies have different quenching effects, and He is a weak collider, while a strong collider would have a significant impact upon the ratio of quenching to bond rupture (reaction 13c).[117]

Very significant mechanistic and kinetic insight has emerged from recent detailed combined experimental and theoretical product studies of radical–radical reactions involving vinyl radicals which will have an important impact upon our understanding of the hydrocarbon reaction systems relevant to both combustion and planetary atmospheric processes.

5.2.2. $C_2H_3 + C_2H_5$

The complexity of the cross-radical reactions of the C_2H_3 and C_2H_5 systems is significantly greater than that involving the CH_3 radical. In the former, the number of reactions and resulting products include the self-combination and disproportionation of both radicals in addition to the combination and disproportionation of the cross-radical reaction, a total of seven reactions. Added interpretive difficulties are caused by the two cross-disproportionation reactions whose products are indistinguishable from the self-disproportionation reaction of ethyl radicals:

$$C_2H_3 + C_2H_5 \rightarrow C_2H_6 + C_2H_2 \qquad (14a)$$

$$\rightarrow 2C_2H_4 \qquad (14b)$$

This, in addition to the expected significant pressure effect on reactions of vinyl radicals, indeed makes this a complex system. The cross-radical combination reaction is exothermic by about 99 kcal/mol,[46] and

$$C_2H_3 + C_2H_5 \rightarrow C_4H_8 \text{ (1-butene)} \qquad (14c)$$

the competition of quenching vs unimolecular dissociation and/or isomerization adds to the interpretive difficulty. There is but a single study, reported by Fahr and Tardy,[120] of the rate coefficient and products of the ethyl–vinyl cross-radical reaction. Vinyl and ethyl radicals in this study have been produced simultaneously through the 193-nm excimer laser photolysis of dilute mixtures of $C_2H_5COC_2H_3$/He. By employing time-resolved UV absorption spectroscopy and analysis of the temporal absorptions of two radicals at 230 and 235 nm through kinetic modeling of the reaction system, an overall rate constant of $(9.6 \pm 1.3) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} resulted. Fitting of the experimental data for the absorption of the two radicals requires knowledge of the rate constants of each individual self-reaction. The argument presented previously, that only monitoring the reactant is necessary for determination of an accurate rate constant, needs some modification to include some measure of the reaction product. The major reaction products, which were identified and quantified using GC/MS analysis, consisted of butane, 1-butene, and 1,3-butadiene which are all formed through the combination reactions $C_2H_5 + C_2H_5 \rightarrow n$-butane, $C_2H_3 + C_2H_3 \rightarrow$ 1,3-butadiene, and $C_2H_5 + C_2H_3 \rightarrow$ 1-butene and ethane, ethylene, and acetylene; the latter three are products of the disproportionation reactions. Using a comparative rate determination method and the yields of the combination products and known self-combination rate constants [$k(C_2H_5 + C_2H_5) = 2.0 \times 10^{-11}$, $k(C_2H_3 + C_2H_3) = 9.3 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}], a rate constant value of $k_{14} = (6.5 \pm 1) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} has been determined for the combination channel of the reaction $C_2H_5 + C_2H_3$.

The effect of pressure on the product channels of the cross-radical reaction $C_2H_5 + C_2H_3$ has been investigated.[121] The yield of the cross-combination product, 1-butene, at various pressures was compared to the yield of n-butane, the combination product of the $C_2H_5 + C_2H_5$ reaction. The $[C_4H_8]/[C_4H_{10}]$ ratio was reduced from ~1.2 at 113 kPa to ~0.4 at 13 kPa. The experimental and simulation results suggest that the observed pressure dependence of $[1\text{-}C_4H_8]/[C_4H_{10}]$ is due to the decomposition of the chemically activated combination adduct $1\text{-}C_4H_8^*$, in which the weaker allylic C–C bond is broken: $H_2C{=}CHCH_2\text{-}CH_3 \rightarrow C_3H_5 + CH_3$, a mechanism that is similar to the $C_2H_3 + CH_3$ reaction. The decomposition of the intermediate occurs even at moderate pressures (~27 kPa) and becomes more significant at lower pressures. The additional products from radical–radical reactions involving allyl, methyl, ethyl, and vinyl radicals were detected at lower pressures.

5.3. Vinyl Radical Reactions with Atoms

5.3.1. C_2H_3 + H/D

Vinyl radicals, produced from the reaction of F atoms with ethylene (reaction 16a, below), have been reacted with H-atoms at low pressure and compared to the reaction of $H + C_2H_5$.[123] The rate constants for the two reactions were found to be comparable, $(5.0 \pm 3.0) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. Acetylene and hydrogen were the only observed products. With D-atoms as the reactant, the products were acetylene and HD.

$$C_2H_3 + D \rightarrow C_2H_2 + HD \qquad (15a)$$

$$\rightarrow C_2H_3D \qquad (15b)$$

At the low pressures of these experiments (0.13−0.25 kPa or 1−2 Torr), the combination to produce ethylene (reaction 15b) was not observed. A value for the sum of both the combination and disproportionation of vinyl with H-atoms in the vinyl iodide photolysis system was obtained by observing the temporal profile of both the vinyl radical and its dimerization product, 1,3-butadiene.[115] The rate constant, (2.0 ± 0.8) × 10^{-10} cm^3 $molecule^{-1}$ s^{-1}, necessitated modeling the mechanism, and the resulting value is in reasonable agreement (within the error bars) of the earlier measurement, recognizing that the former lower value is that of reaction 15a alone. A direct determination of the rate at low pressure (about 130 Pa or 1 Torr) and temperature (213 K) was obtained by Monks et al.,[123] who formed both reactants simultaneously through the F-atom reactions with C_2H_4,

$$F + C_2H_4 \rightarrow C_2H_3 + HF \qquad (16a)$$

$$\rightarrow C_2H_3F + H \qquad (16b)$$

to yield C_2H_3 by abstraction and H-atoms from the displacement reaction that yields $C_2H_3F + H$ (reaction 16b). The rate constants for the nondeuterated versions of reactions 15a and 15b were (1.1 ± 0.3) × 10^{-10} cm^3 $molecule^{-1}$ s^{-1} at 298 K and (1.0 ± 0.3) × 10^{-10} cm^3 $molecule^{-1}$ s^{-1} at 213 K, indicating a near-zero activation energy for the reaction. The overall reaction is presumed to be two separate but competing parallel reactions rather than one that involves a single intermediate that can undergo dissociation or stabilization. Quantum Rice−Ramsperger−Kassel (QRRK) calculations support the mechanistic concept of two competing processes. The mechanism and branching ratio were ascertained by substitution of C_2D_4 as reactant. The assumption is that the mechanism, with its rapid rate constant and a concomitant zero activation energy, is unaffected by isotopic substitution. Within the relatively large uncertainties associated with this determination, two product channels are identified; the combination is found to be about 0.3 of the total reaction over the entire temperature range studied (213−298 K) and the remainder (0.7) due to disproportionation channel 15a. Fahr[124] re-investigated the reaction $C_2H_3 + H$ using excimer laser photolysis of vinyl iodide in conjunction with kinetic absorption spectroscopy and modeling of the reaction system. A detailed error analysis that accounted for the contribution of the random and systematic uncertainties was applied to derive a combined uncertainty. A rate constant value of (1.8 ± 0.43) × 10^{-10} cm^3 $molecule^{-1}$ s^{-1} was determined, which is in excellent agreement with much of the earlier work.

Theoretical studies of the $C_2H_3 + H$ reaction have shown the presence of three separate barrier-less reaction channels.[125] One might imagine three possible H-abstraction reactions, but only one is without a barrier, and that is the abstraction of the CH_2 hydrogen cis to the single CH hydrogen. The abstraction of the CH_2 hydrogen trans to the CH hydrogen has a small barrier, and there is no path at reasonable energies for abstraction of the single CH hydrogen. Two addition channels, one from each side of the radical center, are also without barrier. The predicted rate constants show a small increase with temperature but are in rather good agreement with existing experimental data, depending upon the optimization level used in the calculation. The predicted branching ratios, however, are significantly lower than those found experimentally but are adjustable through modification of the barrier to product elimination.

5.3.2. $C_2H_3 + O$

There has been but a single study of the reaction of vinyl radical with O-atoms, and it was done at low pressure[122] with mass spectrometric sampling of both reactant and products. The rate constant was determined by comparison to the reference reaction of neopentyl radical with O-atoms. The rate constant was found to be equal to (5.0 ± 3.0) × 10^{-11} cm^3 $molecule^{-1}$ cm^{-1}. The mechanism of this highly exothermic reaction can lead to a variety of products, several of which have been observed, including CH_3 radical and ketene (CH_2CO).

$$C_2H_3 + O \rightarrow CH_3 + CO \qquad (17a)$$

$$\rightarrow CH_2CO + H \qquad (17b)$$

The possible reaction leading to $C_2H_2 + OH$ was specifically not observed. Although significant energy is available for dissociation of the products and a peak at $m/e = 14$ (the signature of CH_2) was observed, that was attributed to direct ionization of the molecular products leading to fragments in the ion source of the mass spectrometer.

5.3.3. $C_2H_3 + C$

The mechanism of the $C(^3P) + C_2H_3$ reaction has been studied theoretically, and the possible reaction intermediates have been identified.[126] The study showed the significant complexity of this reaction, as the initially formed C_3H_3 has sufficient energy to either dissociate or isomerize to a wide variety of C_3H_x species. There is no estimate of the rate constant for this reaction.

5.3.4. $C_2H_3 + N$

For some of the outer planets or their moons that have significant N_2-containing atmospheres, the reaction of $N(^4S)$, produced from the interaction of high-energy solar radiation with N_2, with small hydrocarbon radicals may play important roles in the overall chemistry. The reaction with vinyl is such a process, and it has been examined, in detail, at the low pressure of 0.13 kPa (1 Torr).[127] The rate constant determination required use of modeling, but the result, (7.7 ± 2.9) × 10^{-11} cm^3 $molecule^{-1}$ s^{-1}, is quite comparable to those of other reactions of N-atoms with hydrocarbon radicals. There are at least six thermodynamically accessible channels for the reaction, three of which were deduced from mass spectral peaks. The observed products and the respective branching ratios are

$$\begin{aligned} N(^4S) + C_2H_3 &\rightarrow CH_3CN && 0.8 && (18a)\\ &\rightarrow C_2H_2 + NH && 0.16 && (18b)\\ &\rightarrow CH_2CN + H && 0.04 && (18c) \end{aligned}$$

5.4. Reactions of C_2H_3 with Inorganic Radicals

A theoretical study of the potential energy surface and hence mechanism of the reaction of vinyl with OH radicals has been reported.[128] Apparently, eight products may be obtained through the various reaction channels that involve association as well as dissociation processes and isomerizations.

5.5. Reactions with Inorganic Molecules

5.5.1. $C_2H_3 + H_2$

It is interesting that the reaction between vinyl radicals and molecular H_2, which might be of real importance in combustion and has been suggested to be a major source of low-molecular-weight hydrocarbons in planetary atmospheric systems, was not experimentally investigated until recently. An initial estimate[129] of reaction 19 that was based upon a large, but entirely assumed, high-temperature mechanism and associated kinetic arguments suggested a rate constant at 298 K might be about 4.7×10^{-17} cm^3 $molecule^{-1}$ s^{-1} or, expressed with its temperature dependence, $(1.3 \times 10^{-11}) \exp(-3725/T)$ cm^3 $molecule^{-1}$ s^{-1}. In a subsequent article, Weissman and Benson[130] used transition-state theory to arrive at a value for the rate constant of either 9.0×10^{-19} or 5.5×10^{-19} cm^3 $molecule^{-1}$ s^{-1} at 298 K, depending upon the structure of the transition state, either linear or bent at 135°. Expressed with the respective temperature dependence, the values are $(5 \times 10^{-15})(T/298)^{0.7} \exp(-2570/T)$ for the linear case and $(3.24 \times 10^{-14})(T/298)^{0.7} \exp(-3300/T)$ cm^3 $molecule^{-1}$ s^{-1} for the bent transition state.

$$C_2H_3 + H_2 \rightarrow C_2H_4 + H \qquad (19)$$

Callear and Smith studied the addition of H-atoms to C_2H_2 and, in the process, estimated the rate of eq 19 as 1×10^{-17} cm^3 $molecule^{-1}$ s^{-1} at 298 K, within a factor of 3.[131a] In subsequent work,[131b] a value of 2.6×10^{-17} cm^3 $molecule^{-1}$ s^{-1} at 298 K was estimated from a relative rate measurement involving product formation in the mercury-photosensitized formation of H-atoms and their reaction with C_2H_2. This work is clearly not a direct measurement of eq 19 and, as noted by the authors, it is a very complex system.

There is little doubt that a direct experimental measurement of a rate constant is preferable to one that is a semiempirical estimate based upon a model. However, in the absence of direct measurements, and as noted previously, estimates can be useful for modeling purposes. Such semiempirical methods include the bond strength−bond length (BSBL)[132] modification of the bond energy−bond order (BEBO)[133] approach. The former seems to be preferable for those cases that involve H-atom abstraction and seems to provide reasonable estimates of activation energies. Using the BSBL approach, an estimate of $k_{19} = (1.7 \times 10^{-12}) \exp(-4250/T)$ cm^3 $molecule^{-1}$ s^{-1} was obtained,[94] which is significantly lower than the other estimates noted earlier.

A more direct measurement of reaction 19 was done by Fahr et al.,[134] who formed the vinyl radicals from the photolysis of either divinyl mercury or methyl vinyl ketone in the presence of an atmosphere of H_2. The formation of 1,3-butadiene, the combination product of the vinyl radicals, was probed spectroscopically. The system is complex and required a model including the disproportionation and combination reactions of C_2H_3 plus several possible reactions of C_2H_3 with H-atoms produced in reaction 19. As in any modeling process, a choice of rate constants for the competing and known reactions must be made, and the results are dependent upon those choices. The fitting calculations yielded $k_{19} = (3 \pm 2) \times 10^{-20}$ cm^3 $molecule^{-1}$ s^{-1}. Methyl vinyl ketone was also used as the radical precursor for gas chromatographic product studies and comparative rate determination. Here, the competing reactions involved CH_3 radicals that formed CH_4 via abstraction from H_2 as well as C_2H_6 from its self-combination. The results with H_2 were compared to those obtained with He, as only CH_4 or C_2H_4 would increase in the presence of H_2. The results showed that $k_{19} \approx 1 \times 10^{-20}$ cm^3 $molecule^{-1}$ s^{-1}, which does provide some support for the value obtained by the more direct absorption spectroscopy measurement.

At the same time as the experiments on the rate constant were in process, Mebel et al. were carrying out an independent ab initio study of the potential energy surface of reaction 19.[135] The work utilized various theoretical methods including density functional theory (DFT). The reaction was shown to proceed solely through a hydrogen-abstraction process with no transition state, corresponding to insertion followed by dissociation. An activation energy of 10.4 kcal/mol was obtained. Variational transition-state theory (VTST) with tunneling corrections was used to obtain a temperature-dependent rate constant of $(3.68 \times 10^{-20})(T^{2.48}) \exp(-3587/T)$ cm^3 $molecule^{-1}$ s^{-1}, or 3×10^{-19} cm^3 $molecule^{-1}$ s^{-1} at 298 K. Without tunneling, a value of 8×10^{-20} cm^3 $molecule^{-1}$ s^{-1} at 298 K was obtained. The agreement between the experimental data of Fahr et al.[134] and the theoretical result is quite reasonable, considering that the two efforts were done totally independently.

More recently, Knyazev et al.[136] remeasured k_{19} at low pressures of about 0.13−0.7 kPa (1−4 Torr) over a temperature range of 500−950 K using the 193-nm photolysis of vinyl bromide as the radical source, followed by photoionization mass spectrometric probing of the vinyl radicals. The analysis method required measurements at relatively low pressures, and the only loss mechanisms considered were reaction 19 and also possible loss of reactive radicals at the cell wall. The results were expressed as $k_{19} = [(3.42 \pm 0.35) \times 10^{-12}] \exp[(-4179 \pm 67)/T]$ cm^3 $molecule^{-1}$ s^{-1}, or about 3×10^{-18} cm^3 $molecule^{-1}$ s^{-1} at 298 K, which is an order of magnitude more rapid than the calculation by Mebel et al.[135] and about 2 orders of magnitude greater than the experimental measurement noted above. An ab initio calculation done by Knyazev et al.[136] gave frequencies of the transition state that were quite comparable to those reported by Mebel et al.[135] However, the calculations reproduced the experimental values of ref 128 after adjustment of the two lowest frequencies of the transition state and the energy barrier for the reaction to optimize the fit. Not surprisingly, the fitted optimized model agrees with the experimental results albeit a factor of 2 faster and, over the above temperature range, is equal to

$$k_{19} = (1.57 \times 10^{-20})T^{2.56} \times \exp(-2529/T)\ \mathrm{cm}^3\ \mathrm{molecule}^{-1}\ \mathrm{s}^{-1}$$

5.5.2. $C_2H_3 + O_2$

Despite the importance of the reaction of C_2H_3 + O_2 to combustion processes, it is surprising that only a limited number of studies of this reaction have been reported. The first reported study was by Gutman et al.,[137] who in 1984, in two rather comparable papers, obtained rate constant and product information over a broad temperature regime at the relatively low pressures required when using photoionization mass spectrometry for analysis. HCO and H_2CO were observed as the only products of the reaction

$$C_2H_3 + O_2 \rightarrow HCO + H_2CO \qquad (20)$$

over the entire temperature range of 300−600 K, with photolysis of C_2H_3Br as the radical source. The mechanism was presumed to proceed through a four-membered ring of the two O-atoms and the two carbons that then undergoes internal scission of the O−O and C−C bonds to form the products. This mechanism is quite comparable to that proposed previously for the reaction of C_2H with O_2.[48] The rate constant was found to be independent of pressure but with a small negative activation energy and was expressed as $k_{20} = [(6.6 \pm 1.3) \times 10^{-12}] \exp[(250 \pm 100)/RT]$ cm^3 molecule^{-1} s^{-1}, or about $(1.0 \pm 0.2) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Kreuger and Weitz studied the vinyl radical kinetics using a diode laser probe for the time-resolved analysis of the reaction products. In a rather complex system consisting of the photolysis of C_2H_3I as the radical source, the fractional decrease in formation of C_2H_4 product in the presence of added O_2, HCl, and C_2H_6 could be predicted if k_{20} were known.[138] A value of $k_{20} = (1.0 \pm 0.4) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} was obtained, which is in excellent agreement with the earlier value.[132]

In an interesting twist, the value of k_{20} was used to positively identify the carrier of a spectrum in the vacuum ultraviolet as the vinyl radical.[98] The decay of the absorption formed from the photolysis of either $Sn(C_2H_3)_4$ or $Hg(C_2H_3)_2$ in the presence of added O_2 was found to have a rate constant of $(6.7 \pm 2.7) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K, which is in agreement, within the expressed error limits, of the Gutman[137] value and provided support for the assignment of the detected VUV absorption features to the C_2H_3 radical. It is interesting that Benson[139] was unable to observe the reaction of vinyl with O_2 at 298 K, but that position was subsequently[140] modified and attributed to the large exothermicity of the reaction, which would permit the energized intermediate to rapidly decompose, under low-pressure conditions of the experiments, before collisional quenching could occur. More recent experiments by Knyazev and Slagle[141] at temperatures up to 1000 K did not evaluate the nature of the products but did confirm exactly the earlier rate constant determination and expressed the rate parameters as $k_{20} = [(6.92 \pm 0.17) \times 10^{-12}] \exp[(120 \pm 12)/T]$ cm^3 molecule^{-1} s^{-1}. The agreement is remarkable for a kinetics measurement!

The important role of reaction 20 has spawned a number of theoretical studies aimed at predicting both the rate constant as a function of temperature and the products and the mechanism of their formation. The system is quite complex. Westmoreland[142] as well as Bozzelli and Dean[143] applied QRRK theory to calculate rate constants and branching ratios of certain products over an extended temperature and pressure range. In both cases, the mechanism for product formation proceeded through cyclization of the intermediate vinylperoxy radical (C_2H_3OO) to a four-membered ring that dissociates to the H_2CO and HCO products, as noted above. Carpenter[144] used a semiempirical approach in conjunction with ab initio calculations of the potential energy surface and suggested that the assumed mechanism involving formation of a four-membered ring was incorrect, that the process involves cyclization of the C_2H_3OO to a three-membered ring, and that only such a mechanism would allow a calculated rate constant that agreed with experiment. A more detailed ab initio study using DFT and RRKM calculations on the proposed mechanism was carried out by Mebel et al.[145] The most favorable reaction pathway was indeed found to be formation of H_2CO and HCO through a three-membered ring with a rate-determining step that requires migration of one of the O atoms to a C−C bridging position. At elevated temperatures >900 K, O-atom elimination from the C_2H_3OO is predicted to be a competitive channel. At very high temperatures the $C_2H_2 + HO_2$ channel becomes the second most significant. The calculated total rate constant for 300−3500 K at 760 Torr N_2 is $(9.15 \times 10^{-13})T^{0.23} \exp(454/T)$ cm^3 molecule^{-1} s^{-1}.

Using the previous experimental data and the theoretical predictions of products, Wang et al.[146] employed time-resolved Fourier transform IR emission spectroscopy to clarify the reaction pathways. The 248-nm photolysis of C_2H_3Br was used in this study as the source of nonemitting vibrationally cold vinyl radicals. In contrast, the 193-nm photolysis of C_2H_3Br has been shown to form vibrationally excited vinyl radicals on which time-resolved Fourier transform emission spectroscopy allows detection of the vibrational spectrum of the transient.[100] This finding might affect much of the earlier work that used C_2H_3Br as a photolytic source of vinyl radicals. While the vinyl radicals may not have been vibrationally excited with photolysis at 248 nm, the energetics

Table 3. Vinyl Radical Reactions and Recommended Rate Constant Parameters, Based on the Available Reported Studies

reaction	k^a	T/K	P/kPa
$C_2H_3 + C_2H_3 \rightarrow$ products	$(1.2 \pm 0.3) \times 10^{-10}$	298	
$C_2H_3 + C_2H_3 + M \rightarrow C_4H_6 + M$	$(0.95 \pm 0.2) \times 10^{-10}$	298	>6
$C_2H_3 + C_2H_3 \rightarrow C_2H_4 + C_2H_2$	$(0.35 \pm 0.1) \times 10^{-10}$	298	>6
$C_2H_3 + H + M \rightarrow$ products	$(1.8 \pm 0.4) \times 10^{-10}$	298	
$C_2H_3 + CH_3 \rightarrow$ products	$(1.5 \pm 0.3) \times 10^{-10}$	298	
$C_2H_3 + CH_3 \rightarrow C_3H_6 + M$	$(1.2 \pm 0.2) \times 10^{-10}$	298	>13
$C_2H_3 + CH_3 \rightarrow C_2H_2 + CH_4$	$(0.3 \pm 0.1) \times 10^{-10}$	298	>13
$C_2H_3 + C_2H_5 \rightarrow$ products	$(9.6 \pm 1.3) \times 10^{-11}$	298	
$C_2H_3 + C_2H_5 + M \rightarrow C_4H_8 + M$	$(6.5 \pm 1.0) \times 10^{-11}$	298	>26
$C_2H_3 + O \rightarrow$ products	$(5.0 \pm 3.0) \times 10^{-11}$	298	0.13
$C_2H_3 + N \rightarrow$ products	$(7.7 \pm 3.0) \times 10^{-11}$	298	0.13
$C_2H_3 + O_2 \rightarrow$ products	$(1.0 \pm 0.2) \times 10^{-11}$	298	
$C_2H_3 + H_2 \rightarrow$ products	$(3.0 \pm 2.0) \times 10^{-20}$	298	100
$C_2H_3 + HCl \rightarrow$ products	$(1.3 \pm 0.3) \times 10^{-12}$	298	
$C_2H_3 + DCl \rightarrow$ products	$(7.8 \pm 1.6) \times 10^{-13}$	298	
$C_2H_3 + C_2H_2 \rightarrow$ products	2.8×10^{-13}	1000	$\sim 1 \times 10^{-4}$
$C_2H_3 + C_2H_4 \rightarrow$ products	2.2×10^{-13}	298−1000	$\sim 1 \times 10^{-4}$

[a] Rate constants are in units of cm^3 molecule^{-1} s^{-1}, using the modified Arrhenius form $AT^n \exp[-E/RT]$.

strongly suggest that the radical, as formed, has much internal and/or translational energy. The major observed product channel is $HCO + H_2CO$ and the second is, interestingly, $CH_3 + CO_2$, which is the most exothermic of the various possibilities. Other products include CO, which may arise from dissociation of the HCO, and a $H_2C_2O_2 + H$ path. Neither emission from the $C_2H_3O + O$ nor the path that produces HO_2 was positively identified, although they might be of minor import. In all cases the products arise through the proposed three-membered ring.

5.5.3. C_2H_3 +HCl

The bond energy of HCl (103 kcal/mol)[46] is quite comparable to that of H_2 (104 kcal/mol),[46] so the abstraction reaction to form C_2H_4 might be expected to have a comparable rate constant, as the overall exothermicities are comparable. Such a study was done, but the rate constant for reaction with HCl is about 5−7 orders of magnitude larger than that with H_2[138] and is equal to $(1.3 \pm 0.3) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, and that for DCl is equal to $(7.8 \pm 1.6) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. The isotope effect, 1.7 ± 0.8, is consistent with the idea of an early transition state for the reaction; i.e., the HCl bond is not as extended as that of H_2 in the transition state, as suggested by Krueger and Weitz, who did a BSBL calculation[138] of these reactions. Another important factor for the large discrepancy in k_{HCl} is the larger electronegativity of the Cl- vs the H-atoms.

While studying the reverse process, Parmar and Benson[140] used the very low pressure pyrolysis technique and obtained a value for the reaction between C_2H_3 and HCl to gain information on $\Delta H_f(C_2H_3)$. The rate constant, $(5.1 \pm 0.9) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}, is in quite reasonable agreement with that obtained by the more direct study.

5.5.4. $C_2H_3 + Cl_2$

The 193-nm photolysis of vinyl bromide served as the source of vinyl radicals in a study involving photoionization mass spectrometry for analysis.[147] The thrust of this work was to examine the reactions of $R + Cl_2$, where R is a series of unsaturated hydrocarbon radicals, vinyl being one. The reaction of $C_2H_3 + Cl_2$ is essentially temperature independent over the range from 298 to 435 K, and the experimentally determined value is $(8.7 \times 10^{-12}) \exp[(240 \pm 604)/RT]$ cm^3 molecule^{-1} s^{-1}. Subsequent work[100] has shown that the vinyl radical may be excited, and this may be cause for concern.

5.6. C_2H_3 Reactions with Organic Molecules

There have been very few experimental studies of the reaction between C_2H_3 and organic species. The formation of vinyl from the addition of an H-atom produced from the Hg-photosensitized decomposition of H_2 to C_2H_2 (reaction 12) and the products of its subsequent reaction with C_3H_6 have been examined.[148] It was found that the vinyl adds to propylene rather than abstracting a H-atom.

BSBL estimates of H-atom abstraction from several hydrocarbons have been made.[94] Again as noted earlier, while such values do not compare with the accuracy of an experimental determination, such estimates are probably useful for modeling when actual values are not available. The rate constants for the abstraction from CH_4 and C_2H_6 are respectively $(5 \times 10^{-13}) \exp(-4350/T)$ and $(1.6 \times 10^{-12}) \exp(-3200/T)$ cm^3 molecule^{-1} s^{-1}. These values, as noted earlier, have errors in the activation energy term of several kilocalories per mole and an inaccuracy in the pre-exponential of a factor of 2−3.

5.6.1. $C_2H_3 + C_2H_2$

The addition of a vinyl radical to acetylene (eq 21) has been suggested to be a possible route for formation of the first aromatic ring, an important step in initiation of soot formation. Only a few rates of vinyl radical additions have been measured. Callear and Smith[131] produced vinyl radicals from H-atom attachment to acetylene and, through analysis of complex chain reactions, derived a rate constant of $k_{21} \approx 1 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 300 K. Fahr and Stein,[149] using the very low pressure (0.13−1.3

$$C_2H_3 + C_2H_2 \rightarrow \text{products} \tag{21}$$

Pa) pyrolysis (VLPP) method, studied reaction 21 between 1000 and 1330 K. By comparing the product of the reaction, vinyl acetylene (C_4H_4), under conditions of the experiment with the product of vinyl combination,

$$C_2H_3 + C_2H_3 \rightarrow C_4H_6{}^* \rightarrow C_4H_4 + H_2, 2H \quad (22)$$

they derived an Arrhenius expression which depended upon the rate chosen for the vinyl combination (reaction 9). The analysis required using an assumed value for vinyl combination reaction of $k_9 = 3.3 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}.

More recently, Knyazev et al.[150] studied vinyl radical reactions with C_2H_2 (reaction 21) and C_2D_2 (21_d) using laser photolysis−photoionization mass spectrometry. Rate constants were determined under pressure conditions of 0.13−0.52 Pa (1−4 Torr) and from about 600 to 900 K. C_4H_4 was detected as a primary product of reaction 21 and C_4H_3D of reaction 21_d. An Arrhenius expression of $k_{21} = (3.2 \times 10^{-12}) \exp(-3025/T)$ cm^3 molecule^{-1} s^{-1} was derived from this study. By using a revised vinyl combination rate constant of $k_9 = 1.3 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, the VLPP rate data were brought into agreement with results of this more direct rate measurement.

5.6.2. $C_2H_3 + C_2H_4$

The only experimental study of the $C_2H_3 + C_2H_4$ reaction used the VLPP[149] method. The rate constant for reaction 23 was derived indirectly by comparing the reaction products C_4H_6 (eq 23) and C_4H_4 (eq 22)

$$\begin{aligned} &H_2C{=}CH + H_2C{=}CH_2 \leftrightarrow \\ &\qquad H_2C{=}CH_2{-}CH{=}CH_2{}^* \rightarrow \\ &\qquad\qquad H_2C{=}CH{-}CH{=}CH_2 + H \quad (23) \end{aligned}$$

produced under low presssure conditions, and using an assumed vinyl combination rate constant of $k_{22} = 3.3 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, an Arrhenius expression of $(1.05 \times 10^{-12}) \exp(-1560/T)$ was derived. Recommended values of vinyl radical rate constants are listed in Table 3.

6. Summary/Conclusions

The reactions of the C_2 unsaturated hydrocarbon radicals represent an important field of endeavor, relevant to a number of macroscopic reaction media, such as combustion and environmental processes. The available kinetic data for these reactions have been discussed here. Surprisingly, relatively little is known about the reactivities and properties of these species, particularly as a function of temperature and pressure. However, advances may be anticipated since their relatively small size should make them amenable to theoretical investigation and might also permit the direct experimental observation and identification of the reaction intermediates and final products. Such an independent theoretical/experimental agreement and confluence would be a significant advance and would provide the linch-pin for interpretation and improved understanding of all unsaturated hydrocarbon radical chemistry.

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