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Diode laser probes of vinyl radical kinetics: The reaction of C_2H_3 with HCI and DCI

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A tunable diode laser probe is used to measure the rate of reaction of vinyl radicals with HCl and DCl at room temperature. Rate constants for reaction with HCl and DCl are $(1.3 \pm 0.3) \times 10^{-12}$ and $(7.8 \pm 1.6) \times 10^{-13}$ cc/molecule s, respectively. These rate constants are about five orders of magnitude faster than the estimated rate constant for reaction of vinyl radicals with H₂, and potential reasons for these differences are considered within the context of the BSBL (bond strength-bond length) model of atom abstraction reactions. The rate constant for reaction of C₂H₃ with O₂ is determined to be $(1.0 \pm 0.4) \times 10^{-11}$ cc/molecule s, in excellent agreement with a previous determination. Finally, the temperature dependence of the vinyl radical + HCl rate constant is reported. The rate constant is found to decrease by approximately 33% over the temperature range of 278–370 K. This change, however, is within the experimental error of the measured rate constants. From these measurements, an activation energy of -840 ± 1400 (2 σ) cal/mol is obtained.

I. INTRODUCTION

The study of the kinetics of gas phase free radicals remains a topic of current interest and activity. Various timeresolved techniques and static bulb experiments have been employed to determine the rate constants for a wide variety of reactions.¹ One species of particular interest is the vinyl (C_2H_3) radical. In addition to being a prototypical unsaturated organic radical, this molecule is also of interest in the areas of combustion chemistry and the chemistry of planetary atmospheres. Vinyl radicals are thought to be present in acetylene–oxygen flames² and are also believed to play a role in the hydrocarbon chemistry of the Jovian atmosphere.³

Despite the importance of the vinyl radical, relatively little information is available concerning its reaction kinetics. This is due, perhaps in part, to the difficulty in detecting C_2H_3 via standard optical techniques. Recently, however, a weak visible transition has been reported.⁴ Gutman and his co-workers,⁵ employing time-resolved mass spectroscopic detection, have measured rate constants for the reaction of vinyl with O_2 and Cl_2 both at room temperature and above. At room temperature, the rate constant for reaction with O_2 was found to be 1.0×10^{-11} cc molecule⁻¹ s⁻¹, while that for reaction with Cl_2 was twice this value. Finally, based on the absence of detectable products an upper limit of 5×10^{-14} cc molecule⁻¹ s⁻¹ was placed on the rate constant for reaction with *i*- C_4H_{10} .

Callear and Smith have recently published rate constants for reaction of vinyl with H₂ and C₂H₂.⁶ The values were derived from measured product ratios of mixtures of C₂H₂, H₂, and mercury, irradiated at 253.7 nm. The H-atom abstraction from H₂ was determined to have a rate constant (at 300 K) of approximately 2.5×10^{-17} cc molecule⁻¹ s⁻¹ while the rate constant for addition of vinyl to C₂H₂ was larger by a factor of 30.

In this paper we report rate constants for the reaction of C_2H_3 with HCl and DCl at room temperature. The rate of formation of the ethylene product is probed via an infrared

transient absorption technique using a diode laser as the probe source. The rate constant for H-atom abstraction from HCl is considerably larger than those previously estimated for abstraction from H₂ and *i*-C₄H₁₀. A relatively modest (factor of 1.7) isotope effect is observed, with transfer of the lighter isotope occurring more rapidly. These results are found to be consistent with the predictions of a simple model for single atom transfer: the BSBL (bond strength-bond length) model of Bérces and Dombi.^{7,8} A determination of the vinyl + O₂ rate constant, yielding a value identical with that determined previously by Gutman and co-workers, is also reported. Finally, measurements of the temperature dependence of the rate constant infer a small activation energy, possibly negative, and no larger than ~600 cal/mol.

II. EXPERIMENTAL

The experimental technique employed involves the generation of radicals via UV photolysis of a precursor molecule. The time evolution of the products is then probed by means of a tunable infrared diode laser. This technique has wide applicability to the study of radical kinetics, since most radicals and stable molecules exhibit moderate to strong absorptions in the $(3-30\,\mu)$ spectral region accessible by commercially available diode lasers. For the experimental setup to be described shortly, a sensitivity for C_2H_4 of better than 3×10^{13} molecules/cc has been achieved. The tunability and narrow bandwidth ($\sim 3 \times 10^{-4}$ cm⁻¹) of the diode laser, along with the narrow Doppler widths of most molecular/ radical absorptions at low pressures, allows for unambiguous identification of the absorbing species.

The diode laser probe is best suited for studying reactions at low (tens of Torr) pressures since at higher pressures the molecular/radical absorption coefficients will decrease due to pressure broadening. Nonetheless, this technique has been employed to study reactions at pressures as high as 200 Torr.⁹

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In the current studies, vinyl radicals were generatd by KrF (248 nm) excimer laser photolysis of vinyl iodide. Previous studies¹⁰ of the UV photolysis of this molecule, primarily at 254 nm, have shown that the major dissociation channel ($\sim 83\%$) yields vinyl radicals:

$$C_2H_3I \xrightarrow{n\nu} C_2H_3 + I \tag{1a}$$

while a second channel ($\sim 17\%$) yields molecular products:

$$C_2H_3I \rightarrow C_2H_2 + HI. \tag{1b}$$

The reaction of vinyl radicals with HCl:

$$C_2H_3 + HCl \rightarrow C_2H_4 + Cl \tag{2}$$

was then monitored by observing the time-resolved transmission of a diode laser tuned to one of the rotational sublevels of the $v = 0 \rightarrow 1$ transition of the v_1 C-H stretching mode of ethylene; one of the products of reaction.

A diagram of the experimental apparatus is presented in Fig. 1. The unfocused output of a Lambda Physik EMG 101 excimer laser operating on KrF (248 nm, ~170 mJ/pulse) completely fills a flow cell 20 cm in length. The diode laser (Laser Analytics, SP5800) probe was first sent through a mode selection monochromator (Laser Analytics, SP5150) and then counterpropagated through the flow cell at a slight angle with respect to the cell axis. Upon emerging from the cell, the diode beam was focused onto the element of an S.B.R.C. InSb photovoltaic detector, fitted with a broad band (3-4 μ) infrared filter. The amplified output of the infrared detector was then digitized (Biomation 8100 transient recorder), averaged (Nicolet 1170) and stored on disk for further analysis.

The frequency of the diode beam used for probing C_2H_4



FIG. 1. The experimental apparatus. Vinyl radicals are produced by KrF (248 nm) excimer laser photolysis of C_2H_3I . Ethylene molecules, produced upon reaction of C_2H_3 with HCl, are probed with an infrared diode laser.

was estimated to be 3132 cm^{-1} , based upon the monochromator calibration and a 0.06 cm⁻¹ resolution FTIR spectrum of ethylene. The measured extinction coefficient for this transition was 0.034 $Torr^{-1}$ cm⁻¹. To our knowledge, no assignments have been published for the individual rotational lines of the v_1 mode. No effort was made to assign the particular transition employed in the present experiments since such knowledge is not required to extract the desired kinetic information. A few experiments were also carried out at ~970 cm⁻¹ (v_7 band of ethylene) and yielded results identical to those obtained at the higher frequency. The 3132 cm^{-1} probe was found to be preferable, both because of the higher laser power in that region and because of some spectral overlap between vinyl iodide and the most intense ethylene absorption accessible to the 970 cm⁻¹ laser. For experiments involving C₂H₃D production, the diode laser was tuned to a C₂H₃D transition at 3123 cm⁻¹ (probably v_5 mode) with an extinction coefficient of 0.014 Torr⁻¹ cm⁻¹.

In general, the output of a diode laser is multimode. By measuring the transmission of the diode laser through the flow cell when filled with a high (~30 Torr) pressure of ethylene, it was estimated that $\geq 95\%$ of the laser output occurred in the mode absorbed by C_2H_4 . This is important for determining relative signal intensities at a given probe laser energy. The actual signal shapes (rise and fall rates), however, will not be affected by the presence of a nonabsorbed laser mode since the nonabsorbed modes will merely produce a dc offset.

Two flow cells, equipped with either BaF_2 or sapphire windows, were employed in the experiment. The first, used for most room temperature experiments, was constructed from aluminum with an internal diameter of 3.0 cm and a length of 20 cm. For temperature dependent experiments a glass cell 20 cm in length with a 2.5 cm i.d. was used. This cell was constructed with a water jacket surrounding the entire cell body, up to and including the O-ring grooves for the windows. In addition, a helical glass tube leading into the cell was also jacketed for preheating (precooling) the gases. The cell temperature was then maintained by flowing water from a themostated bath through the outer jacket. In addition, heated air or cooled nitrogen was blown across the cell windows in order to maintain their temperature near that of the rest of the cell. For experiments carried out at 370 K, the water jacket was filled with silicon oil, and the cell wrapped with heating tape. Cell temperatures were determined from the temperature of the fluid in the water jacket (employing a standard mercury thermometer) and from measurements taken on the inner walls of the cell using a chromel-alumel thermocouple under conditions identical to the actual experiment but without windows on the cell. The estimated uncertainty in the cell temperature (upon heating or cooling), due to nonuniform heating, was ± 5 K.

Individual components of the gas mixture were prepared in glass bulbs. The flow rates of the components were regulated by the use of Tylan mass flow controllers. The components were then passed through a tube packed with glass beads to ensure thorough mixing before entering the flow cell. Flow rates were such that the gas mixture in the cell was exchanged twice between successive excimer laser pulses. Sample compositions were determined from the relative flow rates of components and the total cell pressure as measured with the MKS capacitance manometer.

Vinyl iodide was prepared by reaction of 1,2-diiodoethane with sodium ethoxide¹¹ and purified by two atmospheric distillations followed by four distillations under vacuum. Gas chromatographic analysis of the product showed it to be 99% pure. Analysis for ethanol (the solvent used in the sample preparation) yielded a concentration of $\leq 0.1\%$.

The following gases with their stated purities were used without further purification: hydrogen chloride (Air Products, Electronic Grade, 99.99%), ethane (Matheson, 99.0%), oxygen (Matheson 99.6%), DCl (MSD, 99 at. % D).

In some experiments, the middle fraction of HCl or DCl withdrawn from a lecture bottle at dry ice temperature was employed. The results were the same as for samples withdrawn directly from the lecture bottle at room temperature. A check of the isotopic purity of DCl passing through the actual flow setup was made by monitoring an HCl transition with the diode laser. Under these conditions a DCl isotopic purity of $\geq 98\%$ was observed.

III. KINETICS

In this section we present the kinetic scheme used to analyze the experimental data. The following processes will be considered:

$$C_2H_3I + h\nu \rightarrow C_2H_3 + I \tag{1a}$$

$$\rightarrow C_2 H_2 + HI, \tag{1b}$$

$$C_2H_3 + HCl \rightarrow C_2H_4 + Cl, \qquad (2)$$

$$C_2H_3 + C_2H_3I \rightarrow C_2H_4 + C_2H_2I$$
 (3a)

$$C_2H_3 + C_2H_3 \rightarrow C_2H_4 + C_2H_2$$
 (4a)

$$\rightarrow C_4 H_6$$
 (4b)

with reaction (3b) representing all the reactions of vinyl with C_2H_3I that do not yield ethylene.

Other radical-molecule reactions, including most of those involving I atoms and the reactions

$$\mathbf{C}_2\mathbf{H}_3 + \mathbf{C}_2\mathbf{H}_2 \rightarrow \mathbf{C}_2\mathbf{H}_4 + \mathbf{C}_2\mathbf{H}_4$$

$$\rightarrow C_4H_4 + H$$

and

$$C_2H_3 + HCl \rightarrow C_2H_3Cl + H$$

can be ignored because of their large (≥ 6 kcal/mol) endothermicities.

The reaction of the photoproducts

 $C_2H_3 + HI \rightarrow C_2H_4 + I$

is energetically possible. However, since the HCl concentration is always considerably larger (150–1500) times than the estimated HI concentration, reaction (2) is expected to sufficiently dominate the above reaction that it can be ignored.

In addition, the above reaction along with reaction (4) involve the collision of two photolytically generated species and are thus bimolecular processes as opposed to reactions (2) and (3) which will be pseudo first order under the ex-

perimental conditions. The importance of bimolecular reactions in the experimental system can be tested by observing the effect of initial photofragment concentration (photolysis laser energy) on the production rate of the ethylene product. For a typical sample mixture [midpoint of the HCl concentration range employed in Fig. 3(a)] the production rate of C_2H_4 was found to remain unchanged, within experimental error, when the excimer laser energy was decreased by a factor of 4.

As a result of the above considerations, a kinetic scheme was developed that includes only steps (1) (treated as instantaneous on the time scale of chemical reaction), (2), and (3). The temporal evolution of ethylene is then given by

$$[C_2H_4] = A [C_2H_3]_0 (1 - e^{-(k_2[HCI] + k_3[C_2H_3I])t})$$
(5)

with

$$A = \frac{k_2[\text{HCl}] + k_{3a}[\text{C}_2\text{H}_3\text{I}]}{k_2[\text{HCl}] + k_3[\text{C}_2\text{H}_3\text{I}]}$$

In the above equations, $[C_2H_3]_0$ represents the initial vinyl radical concentration and $k_3 = k_{3a} + k_{3b}$. Expression (5) thus predicts an exponential growth in the ethylene concentration mirroring the exponential decay of C_2H_3 . This will be the case even if all vinyl radicals do not react to produce ethylene, since the temporal growth of C_2H_4 must reflect the temporal loss of its soul precursor— C_2H_3 . The preexponential factor A is given by the fraction of vinyl radicals that become ethylene molecules, which in turn is equal to the ratio of the rate of C_2H_4 production to the total rate of vinyl radical reactions.

The energy states of the product molecules have not been specified in Eqs. (2) and (3). In general, some fraction of the nascent products will be vibrationally excited and will relax to an equilibrium distribution on a time scale that is characteristic of the particular gas mixture. Thus, expression (5) represents the total concentration of ethylene, summed over all energy states. As the diode laser monitors only the ethylene population in the ground vibrational state (actually the population difference between v = 0 and v = 1), the experimental signals will be described by Eq. (5) only if: either an (experimentally) insignificant fraction of products are produced with vibrational excitation or vibrationally excited products are relaxed on a time scale significantly faster than the time scale for chemical reaction. Various experiments were performed to verify that this was the case. These experiments will be described in the following section.

Finally, it will be useful to generalize the above kinetic scheme by introducing an additional step involving the reaction of vinyl radical with some added scavenger (S) to produce products other than ethylene:

$$C_2H_3 + S \rightarrow . \tag{6}$$

This step must enter into the kinetics in a manner exactly analogous to Eq. (3b) to give

$$[C_2H_4] = A'[C_2H_3]_0(1 - e^{-k't}),$$
(7)

where

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$$A' = \frac{k_2[\text{HCl}] + k_{3a}[\text{C}_2\text{H}_3\text{I}]}{k_2[\text{HCl}] + k_3[\text{C}_2\text{H}_3\text{I}] + k_6[\text{S}]}$$
(8)

and

$$k' = k_2[\text{HCl}] + k_3[\text{C}_2\text{H}_3\text{I}] + k_6[\text{S}].$$
 (9)

As expected, the added scavenger decreases the fraction of vinyl radicals that produce ethylene and increases the decay rate of C_2H_3 . Thus, the effect of the scavenger will manifest itself in both the preexponential (8) and the rate (9).

IV. RESULTS

Figure 2 contains a typical experimental signal. The diode laser intensity is seen to diminish as ethylene is produced in the reaction mixture. The assignment of C_2H_4 as the absorbing species is easily verified by tuning the diode laser slightly off resonance. When the laser is tuned 0.007 cm⁻¹ off resonance, the signal decreases by over an order of magnitude.

Three separate tests were performed to check the validity of the kinetic scheme (Sec. III) employed in obtaining reaction rate constants. The first test involved the addition of ethane to the reaction system to determine whether or not vibrational energy relaxation of C_2H_4 was complete on the time scale of chemical reaction. As mentioned in the preceding section, this is necessary in order to analyze the temporal evolution of the experimental signal via Eq. (5).

Ethane is an efficient vibrational relaxer of C_2H_4 . The rate constant of vibrational relaxation of ethylene by C_2H_6 has previously been determined to be 92.0 ms⁻¹ Torr⁻¹ (2.86×10⁻¹² cc molecule⁻¹ s⁻¹) at room temperature.¹² On the other hand, C_2H_6 is not expected to be an efficient scavenger of vinyl radicals. A previous theoretical estimate of the rate constant for the reaction:

$$C_2H_3 + C_2H_6 \rightarrow C_2H_4 + C_2H_5$$

yielded a value of 3.7×10^{-17} cc molecule⁻¹ s⁻¹ at room temperature.¹³ This value is five orders of magnitude smaller than that measured for Eq. (2) in the present work.

Thus addition of ethane provides a simple test of the



FIG. 2. A typical experimental signal obtained upon averaging for 30 laser shots. As ethylene molecules are produced in the reaction, the transmitted intensity of the diode laser diminishes. The concentrations of the component gases are $[C_2H_3I] = 1.64 \times 10^{16}$, $[HCl] = 1.12 \times 10^{17}$, and $[C_2H_6] = 1.14 \times 10^{17}$ molecules/cc.

influence of vibrational relaxation on the experimental signals. If the ethylene is born predominantly in the ground vibrational state or vibrational relaxation is fast on the time scale of reaction, the addition of ethane will not effect the ethylene transient. However, if a significant number of ethylene molecules are produced in excited vibrational states and relaxation is comparable to or slower than reaction, the addition of ethane will increase the rise rate of the ethylene transient. Eventually, upon addition of a sufficient quantity of ethane, vibrational relaxation will become fast relative to chemical reaction and no further increase in the appearance rate will be observed. Under these conditions, the appearance rate becomes the rate of the reaction of vinyl radicals.

Experimentally, no statistically significant change was observed as the pressure of added ethane was varied from 0 to 10 Torr. To ensure that vibrational relaxation would not be a problem under any experimental conditions, the addition of ethane was carried out near the highest HCl concentration (fastest reaction rate) employed for determining rate constants, since such conditions impose the most severe constraints on vibrational relaxation rates. The independence of ethylene appearance time as a function of added ethane implies that if any C_2H_4 is formed in excited vibrational states, it is relaxed sufficiently rapidly by the C₂H₃I-HCl mixture that vibrational relaxation is not rate limiting. Nonetheless, as a matter of practice, a constant pressure of ethane was added to the reaction mixture for all of the reported determinations of rate constants. This acted as a safeguard against any possible decrease in C_2H_4 relaxation time by C_2H_3I and HCl at temperatures other than room temperature and provided additional heat capacity for the system, thus avoiding significant temperature rises.

As an additional point, it should be noted that the observed insensitivity of signal appearance time to added ethane concentration implies that the rate constant for reaction of C_2H_3 with C_2H_6 is considerably smaller than k_2 . If a 15% uncertainty is assumed for the decay rates obtained from fitting experimental data, then the rate constant for the vinyl + ethane reaction must be less than $k_2/7$. As mentioned previously, various theoretical calculations¹³ predict even smaller values for this rate constant.

Until now, no assumption has been made concerning the energy states of the reacting C_2H_3 radicals. Since the vibrational frequencies of C_2H_3 are in general expected to be similar to those of C_2H_4 ,¹⁴ one would, by analogy with C_2H_4 , expect any vinyl radicals that are formed in vibrationally excited states to be well relaxed on the time scale of chemical reaction. This is a virtual certainty with added ethane.

A second experimental check of the kinetic scheme involves the addition of O_2 to the system as a scavenger of vinyl radicals:

$$C_2H_3 + O_2 \rightarrow HCO + CH_2O. \tag{10}$$

By combining the experimentally observed production rate of C_2H_4 in the absence of O_2 and the previously reported rate constant for Eq. (10) one can predict the fractional change in ethylene yield (signal intensity) upon addition of a given concentration of oxygen. This is given by the ratio of Eq. (8) to the preexponential in Eq. (5):

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fractional decrease

$$=\frac{k_{2}[\text{HCl}] + k_{3}[\text{C}_{2}\text{H}_{3}\text{I}]}{k_{2}[\text{HCl}] + k_{3}[\text{C}_{2}\text{H}_{3}\text{I}] + k_{10}[\text{O}_{2}]},$$
(11)

where the scavenger S in Eq. (6) is now identified as O_2 . If the observed appearance rate of ethylene is equated with the reaction rate of vinyl radicals [the numerator in Eq. (11)] then

fractional decrease of
$$C_2H_4$$

= $\frac{\text{rate without } O_2}{\text{rate without } O_2 + k_{10}[O_2]}$. (12)

The expression "rate without O_2 " represents the rate of appearance of ethylene, under a given set of conditions without added O_2 . The ability of expression (12) to correctly predict the observed decrease in ethylene production upon addition of O_2 is thus a second check of the entire kinetic scheme.

Experiments were performed in which O_2 was added to a mixture consisting of 1.6×10^{16} molecules/cc vinyl iodide, 9.7×10^{16} molecules/cc HCl, and 1.1×10^{17} molecules/cc C_2H_6 . The observed C_2H_4 appearance rate, in the absence of O_2 , was measured as 225 ms⁻¹. This number, along with the reported value of $k_{10} = (1.0 \pm 0.2) \times 10^{-11}$ cc molecule⁻¹ s⁻¹ can be inserted into Eq. (12). The equation then predicts a decrease of 50 \pm 3% in the ethylene signal intensity upon addition of 0.69 Torr O_2 . The quoted uncertainty reflects only that in k_{10} . Experimentally, a decrease of 46% with an estimated uncertainty of ~5% was observed, in excellent agreement with the predicted value.

Equation (9) demonstrates that the value of the rate constant for the reaction of vinyl with O₂ can also be measured by monitoring the change in C₂H₄ appearance rate with added oxygen, at constant C₂H₃I and HCl pressures. Such experiments were performed and a value of $k_{10} = (1.0 \pm 0.4) \times 10^{-11}$ cc molecule⁻¹ s⁻¹ was obtained, in excellent agreement with the previously reported value.⁵ This agreement is particularly encouraging in light of the fact that these two values were obtained from different chemical system via different experimental techniques.

The value of k_2 , the rate constant for the reaction of vinyl radicals with HCl, was next determined from Eq. (5) by varying the HCl concentration at constant vinyl iodide (and ethane) concentration. Experimental signals were fit to a single exponential decay via a nonlinear least squares program.¹⁵ Figure 3(a) contains one of two sets of experimental data used to determine k_2 . The average value of the rate constants from the two sets of data yields $k_2 = (1.3 \pm 0.3) \times 10^{-12}$ cc molecule⁻¹s⁻¹ at room temperature. Figure 3(b) contains the results of a measurement of the rate constant for reaction of C₂H₃ with DCl. In this case a value of $(7.8 \pm 1.6) \times 10^{-13}$ cc molecule⁻¹s⁻¹ was obtained.

As a final check of the internal consistency of the kinetic scheme employed, the experimentally determined value of k_2 can be inserted into the preexponential term

$$A = \frac{k_2[\text{HCl}] + k_{3a}[\text{C}_2\text{H}_3\text{I}]}{k_2[\text{HCl}] + k_3[\text{C}_2\text{H}_3\text{I}]}$$
(13)

of expression (5) to predict the expected change in signal



FIG. 3. (a) The HCl concentration dependence of the ethylene appearance rate at 298 K. This plot is one of the two data sets used to determine $k_2 = (1.3 \pm 0.3) \times 10^{-12}$ cc/molecule s. (b) A similar plot for reaction with DCl at room temperature. The slope of the least squares fit yields a rate constant of $(7.8 \pm 1.6) \times 10^{-13}$ cc/molecule s.

intensity with HCl concentration. The denominator in Eq. (13) is again equated with the ethylene appearance rate. In computing the value of the numerator, only the first term is retained, under the assumption that $k_{3a} \ll k_2$. This is quite reasonable when one considers the expected activation energy for Eq. (3a). A BSBL calculation for H-atom abstraction from *ethylene* by vinyl radicals (assumed to be similar to abstraction from C₂H₃I) yields an activation energy of approximately 6.6 kcal/mol. Thus, even if the preexponential for k_{3a} is gas kinetic (which it most likely is not), one would anticipate a rate constant of only $\sim 10^{-14}$ cc molecule⁻¹ s⁻¹ for Eq. (3a).

Table I contains observed signal intensities (arbitrarily normalized to one for a particular HCl concentration) and their predicted values [from Eq. (13)] over a range of HCl concentrations. The predicted signal intensities are determined using the least squares fit to a particular data set along with the assumption $k_2 \gg k_{3a}$. Observed signal intensities have been corrected for the change in ethylene absorption cross section with total pressure. The agreement between calculated and experimentally observed amplitudes is seen to be quite satisfactory.

The very fact that the observed C_2H_4 signal intensities vary with HCl concentration implies that HCl must be competing for vinyl radicals with some other species in the sys-

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TABLE I. HCl concentration dependence of the C₂H₄ signal intensity.^a

[HC1] $\times 10^{-16}$ (molecules/cc)	Ethylene signal amplitude O predicted by Eq. (13)	served ethylene signal amplitude ^b		
1.60	0.55	0.63		
4.95	1.00	1.00		
8.06	1.19	1.20		
11.2	1.29	1.27		
14.6	1.37	1.31		
17.4	1.41	1.34		

* Conditions: 1.64×10^{16} molecules/cc C_2H_3I and 1.14×10^{17} molecules/cc $C_2H_6.$

^bCorrected for variation in ethylene cross section with total pressure.

tem. In mathematical terms, this implies a nonzero y intercept for plots of the C₂H₃ reaction rate vs HCl concentration. As seen in Fig. 3(a) the y intercept is nonzero. The average intercept obtained from the two determinations of k_2 is $56 \pm 27 \text{ ms}^{-1}$. In the present kinetic scheme, this intercept is interpreted as $k_3[C_2H_3I]$. Dividing by the vinyl iodide concentration, one obtains a value of $k_3 = (3.5 \pm 1.7) \times 10^{-12}$ cc molecule⁻¹ s⁻¹. Measurements of the C₂H₃I concentration dependence of the ethylene appearance rate at constant HCl pressure yields a value approximately 40% smaller than determined from the y intercept. As discussed previously, k_{3a} is expected to be small compared to this derived value of k_3 . With this assumption, $k_{3b} = (3.5 \pm 1.7) \times 10^{-12}$ cc molecule⁻¹ s⁻¹.

As Eq. (3b) implies, no assumption is made concerning the identity of the products of this reaction other than the fact that they do not include ethylene. The reaction could be an addition of the C_2H_3 radical across the double bond of vinyl iodide. The magnitude derived for k_{3b} , however, is surprisingly large in comparison with values previously derived for reaction of C_2H_3 with unsaturated hydrocarbons. Rate constants for reaction of C_2H_3 with C_2H_4 and C_2H_2 have previously been reported as 4×10^{-18} (extrapolated to 300 K)¹⁶ and $\sim 7.5 \times 10^{-16}$ cc molecule⁻¹ s⁻¹ at 300 K,⁶ respectively. The presence of an iodine atom in C₂H₃I might help to stabilize the activated complex relative to those formed upon reaction with C_2H_4 or C_2H_2 , resulting in a larger rate constant. Nonetheless, it is useful to consider other possible contributions to the y intercept other than reaction (3).

Any impurity in the vinyl iodide which scavenges vinyl radicals will increase the y intercept as shown by expression (9). Special attention must be paid to ethanol, the solvent used in preparing C_2H_3I , since its hydroxyl hydrogen might be readily extractable by vinyl radicals. Gas chromatographic analysis of the C_2H_3I , however, revealed an ethanol concentration of $\leq 0.1\%$. At this concentration, reaction with vinyl would contribute only $\sim 5 \text{ ms}^{-1}$ to the intercept even if the reaction rate constant was gas kinetic. Thus, any ethanol impurity could not significantly effect the y intercept. The overall impurity level in the C_2H_3I was found to be approximately 1%. Scavenging by these impurities would have to occur at a gas kinetic rate in order to account for the y intercept. While not impossible, this seems unlikely.

Finally, it should be noted that while the lack of a laser



FIG. 4. An Arrhenius plot of the temperature dependence of k_2 . Also included are the experimental uncertainties of the individual rate constants.

energy dependence of the ethylene appearance rate demonstrates that reaction (4) does not play an important role in the kinetics of the experimental system, it is still possible, within the experimental uncertainty of our measurements, that Eq. (4) occurs to some degree in the chemical system. Such a reaction would contribute to a nonzero y intercept.

In light of the preceding discussion, we choose to interpret the y intercept of Fig. 3(a) as determining an upper limit for k_{3b} of $\leq (3.5 \pm 1.7) \times 10^{-12}$ cc molecule⁻¹ s⁻¹.

A measurement of the temperature dependence of k_2 was perfored over the range of 278-370 K. These results are presented as an Arrhenius plot in Fig. 4. A linear least squares fit to the data yields a negative activation energy of - 840 cal/mol. As can be seen from this plot, however, within the error limits of the experimental points, the activation energy may be either positive or negative. If these error limits are incorporated into the uncertainty of the activation energy, a value of $E_a = -840 \pm 1400(2\sigma)$ cal/mol is obtained. The large percentage uncertainty in the activation energy is due in a great part to the small magnitude of E_a . The rate constants are found to vary by only $\sim 33\%$ over the experimental temperature range of almost 100 K. A conclusion which can be drawn is that the activation energy, if positive, is small (≤ 600 cal/mol) and that it may in fact be negative.

V. DISCUSSION

A. Magnitude of rate constants

The first point of interest concerns the magnitude of k_2 measured in these experiments. This value is several orders of magnitude larger than either the measured or estimated rate constants^{6,13} for H-atom abstraction by vinyl radical from H₂ and various hydrocarbons and it is interesting to consider the possible reasons for these differences. Such large differences are undoubtedly due to differences in activation energies. Thus, a simple model for estimating activation potentials¹⁷ is desirable. The recently proposed BSBL (bond strength-bond length) formulation of Bérces and Dombi^{7,8} is one such model. This model is in many ways

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similar to the BEBO (bond energy-bond order) treatment of Johnston and Parr¹⁸ and various aspects of BEBO can be shown to be special cases of the BSBL formulation.⁷ For the systems of present interest, BSBL is considered preferable in that, in many instances, it has been found to yield more accurate results for atom transfer involving halogens and unsaturated organic radicals as end groups.⁸ Typically the accuracy of predicted activation energies is on the order of 1 to 1.5 kcal/mol.

The BSBL treatment applies to single atom transfer reactions of the type $A + BC \rightarrow AB + C$. The activated complex is treated as a three electron system with energy contributions from: (a) the $A \cdots B$ and $B \cdots C$ bonding energies, (b) stabilization energy due to delocalization of the odd electron over the three atom system, and (c) triplet repulsion between the unpaired electrons on A and C.

The energy contribution from (a) is given as a weighted sum of the Morse potential energies $-V_{AB}$ and $-V_{BC}$ of the atom pairs

$$-g_{AB}V_{AB} - g_{BC}V_{BC}, \qquad (14)$$

where

 $g_{ij} = \exp(-2\beta_{ij}X_{ij}).$

 $X_{ij} = R_{ij} - R_{ij}^{0}$, the *i*-*j* displacement from the equilibrium bond length R_{ij}^{0} in a diatomic *ij* molecule and β_{ij} is the Morse parameter for an *ij* diatomic.

The effects of (b) and (c) are combined into a single term of the form

$$A_{\rm AC}g_{\rm AC}V^0_{\rm AC}.$$
 (15)

The last two factors in this expression are the leading term in a triplet potential function proposed earlier by Bérces¹⁹ with V_{AC}^{0} the classical well depth for the AC Morse function. The first term in Eq. (15), which can be either positive or negative, contains the effect of end group electronegativities on the activation potential. The functional form proposed by the authors is

$$A_{\rm AC} = 2\{\exp[0.75(1 - \overline{\rm EA})] - 1\}$$
 (16)

with EA the average of the electron affinities (in eV) of A and C. The overall BSBL potential expression then becomes

$$V(X_{AB}, X_{BC}) = V_{BC}^{0} - g_{BC} V_{BC} - g_{AB} V_{AB} + A_{AC} g_{AC} V_{AC}^{0}, \qquad (17)$$

where the term V_{BC}^{0} is added to assign the zero of energy to the reactants. The activated complex is assumed to be collinear and thus V is a function of two independent variables X_{AB} and X_{BC} . The authors then choose the reaction path

$$g_{\rm AB} + g_{\rm BC} = 1, \tag{18}$$

rendering V a function of a single variable. The potential can then be maximized along the reaction path to yield the activation potential V^{\ddagger} , where \ddagger stands for the activated complex, and the transition state geometry. While Eq. (17) yields only the reaction potential along a single path, the authors have recently proposed a formulation for the full BSBL surface.²⁰

The results of BSBL calculations of V^{\ddagger} for reaction of vinyl radicals with HCl and H₂ (for comparison) are presented in Table III, where the values of the individual terms in Eq. (17) are also tabulated. The values of the molecular parameters used for the calculation are collected in Table II. From Table III it can be seen that both bonding and end group effects contribute significantly to the difference in V^{\ddagger} between HCl and H₂. In making comparisons, the first three terms in Eq. (17) combine to give the bonding energy contribution to V^{\ddagger} . This sum, which is the bonding energy that must be added to "create" the activated complex is approximately 1.5×10^{-13} ergs larger for the case of H₂ as compared to HCl. Insight into the difference, in turn, can be gained by

Molecular bond	v_0^{a} (cm ⁻¹)	Bond enthalpy (kcal/mol)	V ^{0 a} (kcal/mol)	<i>R</i> ⁰° (Å)	Electron affinity (eV)	R_x^{0} (A)
H-H	4395.2	103.27 ^{d,f}	109.55	0.7416	• • •	
H-Cl	2989.47	102.2 ^{c,f}	106.5	1.2746	• • •	
DCl	2090.78	103.3 ^{c,f}	106.3	1.274		•••
HC,H	3026.4	108.6°	112.9	1.086		3.21
CI-C,H,	720	92.9°	93.9	1.726		3.43 ⁱ
н			•••	•••	0.75 ⁸	•••
Cl				•••	3.61 ^s	

TABLE II. Molecular constants used for BSBL calculations.

*Potential energy of bond dissociation. Estimated as the sum of the zero-point energy and bond enthalpy. See T. Bérces, Acta Chim. Acad. Sci. Hung. 92, 31 (1977).

^b Interatomic distance of the Lennard-Jones diatomic rare gas analog of the molecular bond.

° Values taken from Ref. 26.

 C_2H_3

^d Value taken from: H. Okabe, Photochemistry of Small Molecules (Wiley, New York, 1978).

*Calculated from heats of formation tabulated in Ref. 24.

^fThese values are actually D_0^0 , the bond dissociation energy at 0 K.

*See Ref. 8, Table II, and references therein.

^h W. Lindinger, D. L. Albritton, F. C. Fehsenfeld, and E. E. Ferguson, J. Chem. Phys. 63, 3238 (1975). Calculations carried out using the values 2.2 eV from Table I of Ref. 8 yielded activation potentials that differed by <20% from those obtained using this value for the electron affinity of C₂H₃.

'See Ref. 8, Table I, and references therein.

1.4^h

TABLE III. BSBL calculations for: $V + HX \rightarrow VH + X$ ($V = C_2H_3$).

	X = H	X = Cl
V [‡] (kcal/mol)	7.89	2.14
V ⁰ _{HX}	76.1	74.0
$-g_{HX}V_{HX}^{*}$	- 45.8	- 63.2
$-g_{\rm HV}V_{\rm HV}^{\rm a}$	- 24.7	- 6.74
Xvx VVx Avx*	- 0.148	- 2.53
V ⁰ _{VX}	78.5	65.3
Avy	- 0.109	- 1.35
Rvy	0.0172	0.0287
X ¹ / _L (Å)	0.277	0.550
X [‡] _{HX} (Å)	0.1201	0.0408

* In units of 10⁻¹³ ergs.

comparing the sum of the first two terms in Eq. (17) which represent the energy needed to stretch the BC bond from equilibrium to its transition state bond length, to the third term-the energy "gained" by creating an (extended) AB bond. As can be seen from the bond displacements in the activated complexes in Table III, both transition states occur rather early. The extension of the H-H bond in vin $yl \cdots H \cdots H$ is about 0.12 Å while the H-Cl extension in vinyl \cdots H \cdots Cl is only 0.04 Å. Since the H \cdots H bond in its transition state is extended three times further form equilibrium than for HCl in its transition state, significantly more energy must be added to "stretch" the H-H bond to the activated complex geometry in the H₂ reaction. Although the $C \cdots H$ bond in viny $\cdots H \cdots H$ is further developed than in vinyl...H...Cl it is still well extended (compared to C_2H_4), and the energy gained in its formation cannot adequately compensate for the significant cost in energy of extending the H-H bond. Thus the more developed vin $yl \cdots H \cdots H$ transition state requires more bonding energy.

The last term in Eq. (17) (end group contribution) also plays an important role in determining the activation potentials. While the magnitude of this term is the smallest of the four in Eq. (17), the valid comparison is between the sum of the first three terms, and this last one. It should first be noted that the end group contribution is negative, for both reactions, implying that resonance stabilization outweighs triplet repulsion effects, thus diminishing the value of V^{\ddagger} . This stabilization effect is larger, by about 2.4×10^{-13} ergs, in the case of HCl as compared to H₂. This difference in the value of Eq. (15) is due primarily to the larger magnitude of A_{AC} for HCl vs H₂. The more negative value of A_{AC} can be directly ascribed to the larger electron affinity of Cl as compared to H.

Thus, within the context of the BSBL model, two important factors in the more rapid reaction of vinyl radicals with HCl (vs H₂) are the larger electronegativity of Cl (vs H) and the earlier transition state of the activated complex containing H…Cl. The above discussion should not be construed as implying that the experimental results somehow verify all of the comparisons made. The preceding discussion is simply the *model*'s explanation of the results. It is possible that the actual magnitudes of V^{\ddagger} obtained results from fortuitous cancellation between the individual terms in Eq. (17), thus obscuring the significance of their values. However, the previous success of this model, when applied to a variety of reactions,⁸ would argue against this.

Finally, it should be noted that, given the expected error in BSBL calculations, the value of V^{\ddagger} obtained for the vinyl + HCl reaction is not inconsistent with the weak temperature dependence of k_2 observed experimentally.

B. Isotope effects

The experimentally determined isotope effect for Eq. (2), $k_{2\rm H}/k_{2\rm D}$, is found to be 1.7 ± 0.8 . This relatively modest isotope effect is consistent with the idea of an early transition state for reaction (2). In general, isotope effects are expected to be most significant in highly developed transition states, with maximum effects anticipated when $X_{\rm AB}^{\dagger} \simeq X_{\rm BC}^{\dagger}$.²¹ On the other hand, as $X_{\rm BC}^{\dagger} \rightarrow 0$ the isotope effect approaches unity. As mentioned previously, the BSBL model predicts an early transition state for the vinyl + HCl reaction.

A transition state theory (TST) calculation of k_{2H}/k_{2D} was carried out using the BSBL geometry. An isotope effect of approximately one was obtained. While agreement with experiment is not entirely satisfactory, it must be noted that the experimental uncertainty in the isotope effect is fairly large, due to the compounding of errors in the two measured rate constants. Also, for an activation potential of 2.1 kcal/mol, the zero-point energy of HCl is larger than the barrier height, a situation in which TST is not always successful.²² Finally, disagreement may be a result of errors in the transition state geometry; perhaps the true transition state is somewhat more "developed" than predicted by the BSBL model. However, it should be realized that the observed modest isotope effect *is* at least qualitatively consistent with the predictions of the BSBL model.

C. Temperature dependence

A final point to be considered concerns the temperature dependence of k_2 . Figure 4 demonstrates that the chief conclusion to be drawn is that the rate constant remains substantially unchanged over a 100 K range and thus the activation energy is relatively small. While a least squares fit to the data implies a small negative activation energy, it has already been pointed out that the experimental uncertainty is larger than the activation energy itself and thus its sign cannot be determined unambiguously from these studies.

It is interesting to note that studies⁵ of the temperature dependence of the reaction of C_2H_3 with O_2 and Cl_2 have yielded small negative activation energies. In the case of Cl_2 , however, the experimental uncertainties were again larger than the value of the activation energy itself. For these systems the potential importance of long range forces and the possibility of a highly polar transition state have been considered.⁵ These effects may also play a role in determing k_2 . If this is the case, a more complex potential function may be required to fully describe the reaction dynamics. Bayes and co-workers²³ have proposed a highly attractive potential function in their treatment of reactions of alkyl radicals with O_2 via the adiabatic channel model. It is thus possible that the BSBL model is not sufficiently complex to describe all of the details of the C_2H_3 + HCl reaction. At the very least,

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however, the model has been demonstrated to successfully predict a significant decrease in V^{\ddagger} for reaction of vinyl radicals with HCl as compared to H₂. In addition, the model predicts an early transition state for C₂H₃ + HCl, consistent with the small isotope effect observed.

As a final point, the exothermicity of $5.6 \pm 2.0 \text{ kcal/mol}$ for reaction (2) (derived from heats of formation²⁴) along with the experimental determination of $E_a < 0.6 \text{ kcal/mol}$ for this reaction allows one to derive an upper limit of $6.2 \pm 2.0 \text{ kcal/mol}$ for the reverse reaction

 $Cl + C_2H_4 \rightarrow HCl + C_2H_3$.

Unfortunately, this reaction is not observed near room temperature due to the occurrence of the more rapid atom addition reaction²⁵:

 $Cl + C_2H_4 \rightarrow ClC_2H_4^*$.

D. Energy disposal

As discussed, experimental results suggest relatively little vibrational excitation in the ethylene produced via reaction (2). The primary reason for this can be found in the small exothermicity $\Delta H_2 = -5.6 \pm 2.0$ kcal/mol of Eq. (2). Thus, if the reacting vinyl radicals are internally relaxed, no more than 1960 cm⁻¹ of energy can be channeled into ethylene vibrations.

Without any further information regarding the details of energy disposition in this system it is reasonable to assume it would be statistical. Ethylene has a rather low density of vibrational states at energies below 1960 cm⁻¹ since its lowest vibrational state is at $810 \text{ cm}^{-1.26}$ Thus, a statistical distribution of energy among all degrees of freedom would predict very little disposition of energy in the vibrational degrees of freedom of ethylene. With only 1960 cm⁻¹ of energy available it is not surprising that little vibrational excitation is observed in the ethylene product.

VI. CONCLUSIONS

The rate constant for reaction of C_2H_3 with HCl has been measured and found to be $k_2 = (1.3 \pm 0.3) \times 10^{-12}$ cc molecule⁻¹ s^{-1.27} For reaction with DCl a value of $(7.8 \pm 1.6) \times 10^{-13}$ cc molecule⁻¹ s⁻¹ was obtained. From the point of view of the BSBL model, the large value of k_2 compared to that for vinyl + H₂, can be ascribed to such factors as the higher electronegativity of Cl (relative to H) and the earlier transition state for Eq. (2). An early transition state is also compatible with the relatively small isotope effect (1.7) measured for reaction (2).

The temperature dependence of k_2 over the range 278– 370 K was also measured and found to be small, with a decrease of $\sim 33\%$ over this range. From these measurements, an activation energy of -840 ± 1400 cal/mol was derived. If the activation energy is in fact negative, this would imply that long range forces may play a significant role in the reaction dynamics.

Finally, a rate constant of $(1.0 \pm 0.4) \times 10^{-11}$ cc molecule⁻¹ s⁻¹ was obtained for the vinyl + O₂ reaction, in excellent agreement with a previous determination employing both a different chemical system and a different experimental technique.

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- ²⁷David Gutman has informed us that he has recently measured the rate of reaction of HCl with vinyl radical via mass spectrometric monitoring of the reaction. The rate constant determined via this method agrees very well with our reported number.

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