Collisional Quenching of Excited Vinylidene (³B₂) Radicals

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Rate constants for the removal of excited-state vinylidene D₂CC (³B₂) in the presence of He, Ar, N₂, H₂, CO, and CH₄ are reported at room temperature. The excited vinylidene radicals are generated via vacuum-ultraviolet photolysis of mixtures of C_2D_3Cl in the quencher gases through the reaction sequence $C_2D_3Cl \rightarrow C_2D_3Cl^* \rightarrow D_2CC(^3B_2) + DCl$. Excited triplet vinylidene radicals are then collisionally quenched to the singlet ground state which undergoes rapid isomerization to acetylene. Rate constants for removal of $D_2CC(^3B_2)$ by quenchers are determined by observation of the time-resolved absorption of either $D_2CC({}^{3}B_2)$ at 137 nm or product C_2D_2 at 151 nm. The observed quenching rate constants for the deuterated species are $k_{\text{He}} = (1.9 \pm 0.3) \times 10^{-15}$, $k_{\text{Ar}} = (6.64 \pm 0.3) \times 10^{-15}$, $k_{\text{N}_2} = (8.5 \pm 0.2) \times 10^{-15}$, $k_{\text{H}_2} = (33.8 \pm 6.1) \times 10^{-15}$, $k_{CO} = (28.0 \pm 8.0) \times 10^{-15}$, and $k_{CH_4} = (28.0 \pm 8.0) \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. No evidence for chemical reaction could be observed. The derived quenching cross sections are correlated with the potential well depth model. This correlation is valuable in predicting nonreactive collisional cross sections for additional gases.

Introduction

Standards

Previously it has been demonstrated in this laboratory that electronically excited vinylidene radicals, H_2CC (³B₂), can be prepared by the vacuum-ultraviolet flash photolysis of several hydrocarbons^{1,2} and a few of its properties and characteristics have been investigated experimentally^{1,3} and theoretically.^{3,4} However, detailed understanding of the chemistry of these radicals remains to be examined. The ground-state singlet vinylidene has a very short lifetime, calculated to be less than 10⁻¹¹ s toward rearrangement to acetylene,⁴ a value recently verified experimentally.⁵ In contrast, electronically excited triplet vinylidene has a long lifetime in the absence of collisions, in part due to the large barrier to isomerization, and thus may be of importance when considering gas-phase chemistry of vinylidenes.

It has been demonstrated recently that the photodissociation of vinyl chloride, in the presence of a diluent, proceeds through an excited long-lived triplet state, probably the $3(\pi,\pi^*)$ state of vinyl chloride.⁶ Dissociation of the excited triplet state, through a spin-allowed elimination, results in the formation of $H_2CC({}^3B_2)$ and HCl, viz.

$$C_2H_3Cl \rightarrow H_2CC (^3B_2) + HCl (^1\Sigma)$$
(1)

The time history of HCl in flash photolysis experiments consists of a pressure-dependent, single-exponential rise with a rate constant of $(1.1 \pm 0.1) \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹. Similarly, the temporal profile of H_2CC consists of a rise, with a rate constant of (1.2 \pm 0.4) \times 10⁻¹³ cm³ molecule⁻¹ s⁻¹, followed by an exponential decay with a time constant of 1.07×10^{-14} cm³ molecule⁻¹ s⁻¹. The rise rates of H₂CC and HCl, within experimental error, are identical. Acetylene, whose absorption is well-known, was absent initially from the photodissociation products and its formation followed a slower time history with a production rate equivalent to $1 \times$ 10^{-14} cm³ molecule⁻¹ s⁻¹, comparable to the decay rate of vinylidene. On the basis of these observations the decay of vinylidene was attributed to collisional quenching of the triplet state to the singlet ground state, which itself would rapidly isomerize to acetylene. It also has been shown that the deuterated vinylidene $({}^{3}B_{2})$ is quenched by He with a rate constant of about 2.4 × 10⁻¹⁵ cm³ molecule⁻¹ s⁻¹, ¹ representing an isotope effect of $k_{He}{}^{H}/k_{He}{}^{D}$ = 5.4. In the photolysis of vinyl chloride, identical production rates (or concentrations) for HCl and H₂CC (³B₂), at times short compared to the quenching of the vinylidene, had allowed the quantitative measurement of the concentration of H_2CC (³B₂) by calibration against the product HCl concentration. When this

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method was used, an extinction coefficient of $694 \pm 218 \text{ cm}^{-1} \text{ atm}^{-1}$ for absorption of H_2CC (³B₂) at 137 nm was obtained.⁷

In the present contribution we report the collisional quenching rate constants of D_2CC (³B₂) radicals with He, Ar, N₂, H₂, CO, and CH4 using the same vacuum-ultraviolet flash photolysis technique as before. To make more accurate rate measurements with the present apparatus and allow slower removal rates of the vinylidene, deuterium-substituted vinyl chloride is chosen as a source of the radical. As will be shown, the experimentally determined quenching cross sections could be correlated with a potential well depth model.

Experimental Technique

The experimental arrangements and techniques used to measure the quenching rates of the excited vinylidene radicals are essentially the same as those previously described^{2,6} and will be summarized here. The experiments were performed by flash photolysis of deuterated vinyl chloride at wavelengths greater than 155 nm, the Suprasil cutoff, followed by kinetic spectroscopy in the vacuum ultraviolet. A Suprasil photolysis cell was placed inside a chamber in which a bank of six capacitors were discharged through N_2 , with a flash duration of about 5 μ s. Spectroscopic analysis was performed with a Garton-type flash lamp of about 2-µs pulse width with essentially continuous wavelength output in the vacuum ultraviolet. Emission lines in the source provided wavelength calibration. The monitoring flash was triggered at a preset delay after the photolysis flash. The output of the analysis flash, from 120 to 185 nm, was focused through LiF optics into a 30- μ m slit of a 2-m focal length, Eagle vacuum spectrograph with dispersion of 2.77 Å/mm at the exit. Spectra were recorded on Kodak SWR plates. Plate transmission data were obtained by densitometry coupled with previously determined characteristic curves of the plate response.

When He, Ar, N_2 , or H_2 was used as a quencher, the rates of depletion of vinylidene $({}^{3}B_{2})$ radicals were monitored by its absorption at 137 nm. However, when CH₄ or CO were collision partners, strong absorption by those molecules in the 137-nm region would interfere with that of vinylidene. In these two cases, the absorption of acetylene at 151 nm was used to indirectly

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Figure 1. Temporal dependence of D_2CC (³B₂) decay with added H₂.

monitor the behavior of vinylidene radicals, recognizing that the production rate of acetylene, within our experimental error, is identical with the depletion rate of vinylidene. Even then, a maximum pressure of about 2 Torr of these gases could be used before their absorption interferred with the acetylene absorption. To prevent the diffusive removal of the fragments out of the path of the monitoring beam, a constant pressure of He (4 Torr) was added to all the sample mixtures when CO or CH₄ was used as the quencher. In a typical experiment, a dilute, premixed gas sample of vinyl chloride in the quencher gas was first admitted into the cell, and if desired, additional quencher gas was added from a higher pressure reservoir. In all the sample mixtures, the partial pressure of vinyl chloride was kept constant (30 mTorr) and the pressure of quenching gas was varied. Adequate time was provided for mixing.

When H_2 , N_2 , and CH_4 were used as quenchers of triplet vinylidene, the possibility of chemical quenching was considered and gas chromatographic analyses (flame ionization detector) of products were carried out. This was done by rapid withdrawal of the post flash sample from the center of the reaction cell. through a small stainless steel tube, and direct injection into the chromatograph columns. Deuterated vinyl chloride with an isotopic purity of 99.7% was obtained from Merck and freeze-thawed before using. Ultrahigh-purity He (99.999%), Ar (99.99%), N₂ (99.999%), and H₂ (99.99%) were used without further purification.

Results and Discussion

The decay rates of vinylidene radicals (or the concomitant production of acetylene) with a certain pressure of collision partner were monitored initially by variation of the delay time between the photolysis and monitoring flashes. The rate measurements were carried out for several pressures of the quencher. The temporal profile of D_2CC (³B₂) was characterized by a rapid exponential rise of at least an order of magnitude greater than the subsequent decay. Experimental conditions always were chosen such that the rise could be neglected, and the decay of vinylidene was analyzed as a single exponential. The production of acetylene in these experiments also fits a single exponential rise which corresponds, within experimental error, to the exponential decay of vinylidene. Quenching rate constants were then obtained from the slope of the least-squares fits of the plots of decay rates vs. pressures of quenchers.

The data have been analyzed assuming that both quencher gas and remaining vinyl chloride ($\sim 50\%$ of original 30 mTorr plus products of the photolysis) quench the excited vinylidene; therefore, $\tau^{-1} = k_{\rm M}[{\rm M}] + k_{\rm C_2D_2} [{\rm C_2D_2}] + k_{\rm C_2D_3Cl} [{\rm C_2D_3Cl}] + k_{\rm DCl} [{\rm DCl}].$ The partial pressures of vinyl chloride in all the samples were kept identical and small relative to the pressure of the quencher. Therefore, the slope, from plots of the observed rates vs. quencher pressure, gives the rate coefficient of the quencher M, with the intercept being the contribution of collision partners other than the quencher gas.



Figure 2. Pressure dependence of $D_2CC({}^3B_2)$ decay with added He, Ar, N_2 , and H_2 .

TABLE I: Absolute Rate Constants (×10¹⁴ cm³ molecule⁻¹ s⁻¹) Relative Rate Constants, and Average Cross Sections ($Å^2 \times 10^3$) for D₂CC (³B₂) Quenching

М	k	$k_{\rm M}/k_{\rm He}$	σ^{a}
He	0.19 ± 0.03	1	0.35
Ar	0.66 ± 0.03	3.47	2.60
N_2	0.85 ± 0.02	4.46	3.12
H_2	3.38 ± 0.61	17.79	4.5
CŌ	2.80 ± 0.80	14.73	10.2
CH₄	2.80 ± 0.80	14.73	8.7

 ${}^a\sigma = k(8kT/\pi\mu)^{1/2}.$

Figure 1 depicts the time-dependent absorption (or concentration) of $D_2CC({}^3B_2)$ for different pressures of H_2 . Similar plots were obtained for other quenchers studied here. For all six collision partners, decay rates of $D_2CC({}^3B_2)$ (or again the rise rate of C_2D_2) were found to obey pseudo-first-order kinetics and increased linearly, within our experimental error, with the pressure of the added gas. Figure 2 shows measurements of the observed decay rates of $D_2CC({}^3B_2)$ in the presence of He, Ar, N₂, and H₂. Rate constants for the quenching of triplet vinylidene by all six collision partners were determined by a linear least-squares fit of the observed rates. In these experiments, no evidence of chemical reaction even at higher concentrations and pressures was observed when H₂, N₂, or CH₄ were used as quenchers. The minimum detectable concentration of hydrocarbon products, through C_4 , was less than 1 mTorr by chromatographic analysis and represents about 10% of the maximum concentration of vinylidene that was determined, in all cases, by its absorption at 137 nm. Attempts to observe HCN via its strong vacuum-ultraviolet absorption were similarly unsuccessful although concentrations as small as 2 mTorr would be within our detection limits. The absence of reaction, at least with H_2 or CH_4 , agrees with predictions of a slow rate constant for abstraction based upon a BEBO model.⁶

The measured absolute quenching rate constants, relative rate constants, and averaged collisional cross sections for removal of $D_2CC({}^3B_2)$ are listed in Table I. Listed uncertainties represent one standard deviation from the least-squares fit of the data. A rate constant of 1.07×10^{-14} cm³ molecule⁻¹ s⁻¹ for quenching of protonated vinylidene radicals with He has been reported previously.⁶ An isotope effect of $k_{(H)}/k_{(D)} = 5.6$ is observed in the present studies. This agrees with an earlier quenching rate measurement of protonated and deuterated vinylidene with He where triplet vinylidene radicals were formed from the photolysis

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of acetylene¹ and an isotope effect of 5.4 was obtained. The present results are the only quenching rate measurements reported for excited-state vinylidene. Therefore, no direct comparison can be made with other experimental or theoretical rate measurements.

The prototypical unsaturated biradicals CD₂ and CH₂ have been the subject of a large number of experimental and theoretical investigations of their chemistry and properties of both ground $({}^{3}B_{2})$ and excited $({}^{1}A_{1})$ states.¹²⁻¹⁵ As in the case of vinylidene, quenching of excited methylene to the ground state requires a forbidden S-T transition. In comparison with our results for vinylidene, the absolute rate constants for removal of CH_2 (¹A₁) by He are about 2 orders of magnitude larger than that for vinylidene. The comparison of the relative rate constants for vinylidene and methylene radicals shows a more significant increase in the rate constant of vinylidene quenching with increasing mass of the inert collision partner (He, Ar, and N_2). In addition, essentially no isotope effect is observed in the quenching of CH₂ $({}^{1}A_{1})$ and CD₂ $({}^{1}A_{1})$ by the rare gases.⁹

Several attempts have been made to explain the unusually rapid quenching rates of methylene $({}^{1}A_{1})$ and the lack of an isotope effect in its quenching.¹⁰⁻¹² Calculations of the direct collisioninduced intersystem crossing,9 intersystem crossing through complex formation,¹⁰ and a mixed-state model^{11,12} have been successful in explaining the rapid quenching rate constants. However, these models predicts a pronounced isotope effect in quenching of ${}^{1}A_{1}$ methylene. The lack of an isotope effect in the experimental observations can only be explained if there is an accidental similarity in the relative positions of the singlet and triplet energy levels for CH₂ and CD₂.

In the case of vinylidene, calculations of Schaefer et al.^{13,14} indicate that triplet vinylidene is well-defined minimum on the same potential surface as triplet acetylene, as is singlet vinylidene on the singlet acetylene surface. The energy levels of triplet vinylidene are expected to be energetically far-removed from those of the ground singlet which would effectively minimize possible spin-orbit coupling. The probability of radiationless transitions between singlet and triplet surfaces involves a variety of factors including the energy separation between the states. In the case of vinylidene the magnitude of the calculated energy gap overwhelms other factors, including the spin-orbit coupling constant, so that the probability of mixing is minimized. As a result, there is no crossing between the ground singlet and excited triplet state in the absence of collision. The deuterium isotope effect observed for quenching of vinylidene and the ratio of the rates in going from He to Ar are in agreement with the expected behavior of the system.¹

The very fast observed quenching rates of CH_2 (¹A₁) with H₂, CH_4 , and N_2 are attributed, in part, to significant contribution of chemical reactions of these collision partners with methylene radicals.^{15,16} In the quenching of vinylidene, within the sensitivity of our techniques, no evidence of chemical reactions was detected as noted previously. However, two other collisional schemes need to be considered in the quenching of vinylidene, namely rotational and vibrational relaxation of the initially formed vinylidene $({}^{3}B_{2})$. Rotational relaxation of excited vinylidene is expected to be very rapid, and the relative efficiencies for rotational relaxation of hydrogen containing molecules, such as hydrocarbons, by rare gases is expected to be more efficient with He than with Ar,¹⁶ the effect opposite to that observed here. Vibrational relaxation within the triplet electronic state of vinylidene also appears unlikely. Again the relative quenching efficiencies by the rare gases are in the opposite order to that expected for vibrational relaxation,¹⁶ and the nonchanging orders of the spectrum with time and pressure support the assignment of the spectral carrier as a vibrationally relaxed entity. In those cases where chemically reactive



Figure 3. Plot of the observed quenching cross sections ($\sigma_{Q,M}$) for D₂CC as a function of $(\epsilon_{\rm MM}/k)^{1/2}$ according to the model of Parmenter (ref 20).

quenching processes are absent, the fate of the collisionally quenched $({}^{3}B_{2})$ vinylidene is likely to be conversion to singlet ground state followed by the rapid isomerization to acetylene. As noted previously, supporting evidence for this argument is the similarity between the observed production rate of acetylene and quenching rate of vinylidene.

The collision-induced quenching of excited molecules or radicals has varying degrees of efficiency depending upon the nature of the excited species and of the collision partner. Over the last 5 decades, several methods and models have been developed to correlate, theoretically, electronic quenching efficiencies with molecular properties, such as permanent dipole moment, polarizability, ionization potential, and the intermolecular potential well depth.¹⁷⁻²⁰ The earliest attempt in this direction was made by Rossler,¹⁷ who proposed that the quenching cross section (σ_Q) was directly proportional to the dipole polarizability (α) of the quencher and the duration of the collision between the excited molecule and the quencher, i.e., $\sigma_{0,M} \propto \alpha_M \mu^{1/2}$ where μ is the reduced mass of the collision pair. Later, Selwyne and Steinfeld¹⁸ proposed a dispersion force perturbation model which assumes mixing of the initial and final states of the excited molecule and quenching partner system. They find the cross sections obey $\sigma_{\rm Q,M} \propto A \mu^{1/2} I_{\rm Q} \alpha_{\rm Q} / R_{\rm e}^3$ where A is a constant that depends on the molecule and the excited state being quenched, μ is the reduced mass, I_0 is the ionization potential, α_0 is the polarizability of the quenching molecule, and R is the minimum impact parameter. These two simple models have been relatively successful in describing quenching by nonpolar molecules.

We attempted to correlate the observed quenching rates for vinylidene with different molecular parameters described by these models. The most successful approach was the potential well depth model developed by Parmenter.²⁰ This model is suggested for describing rapid processes and assumes that interactions leading to the state change must involve predominately long-range attractive forces. The model considers formation of an intermediate complex (A*-M) in equilibrium with the separated species. A calculation of the transition-state concentrations from partition functions can lead to correlations between the cross sections and the attractive well depth (ϵ_{A^*-M}) of the metastable complex formed by collision. With the assumption of $\epsilon_{A^*-M} \propto (\epsilon_{MM})^{1/2}$ they give

$$\ln \sigma_{\rm Q,M} = \ln C + \beta \left(\frac{\epsilon_{\rm MM}}{k}\right)^{1/2}$$

where C is a constant and β is a temperature-dependent factor that depends only on A^* and is therefore constant for a series of M. This well depth model has been applied to describe a variety of collisional relaxation systems. Figure 3 shows the correlation

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plot of $\ln \sigma_{\rm OM}$ vs. $(\epsilon_{\rm MM}/k)^{1/2}$. $\sigma_{\rm QM}$ is the quenching cross section for the D₂CC (³B₂) with collision partner M, and ϵ_{MM} is the well depth in the attractive potential between the pairs of M species. The values of $(\epsilon_{MM}/k)^{1/2}$ are taken from ref 20. A linear relationship between these parameters is shown in Figure 3. Notably, in this case, the best fit to the data results in a line through the points for species in which no chemical reaction can occur, e.g., the inert gases, and a correlation coefficient of close to 1.0 is obtained. However, as noted previously, we were unable to discern any chemical reaction between triplet vinylidene and either H₂ or CH₄. In the absence of evidence of direct chemical reaction, we attribute the observed removal of triplet vinylidene to physical quenching. The least-squares fit, shown in Figure 3, through all the data points has a correlation coefficient of 0.78. Several molecules for which a reactive channel may exist have data points that fall above the line. We have noted previously that a maximum of 10% of the vinylidene may react chemically with H_2 . Even if we correct the rate constant for quenching of the D_2CC (³B₂) by H_2 , the maximum contribution due to chemical reaction, the single point for H₂ remains slightly above the least-squares line in Figure 3. Further, the predicted rate constants for abstraction from CH_4 are quite comparable to that from H_2 .⁸ Yet, the cross section for quenching by CH₄ does correlate well with the well depth model. The correlation may indicate that interactions involving attractive forces are significant for quenching processes in vinylidene. It appears that this correlation method can be successful in describing quenching processes with rate constants slower than gas kinetic collision rates.

The model suggests that we sample the long-range attractive forces as the two species approach each other. Both the ${}^{3}B_{2}$ and ${}^{1}A_{1}$ states of D₂CC have similar equilibrium geometries, and hence the respective potential energy minima would lie essentially directly above one another, separated by the energy gap. However, the singlet has only a 2 kcal/mol barrier to isomerization to acetylene. In these circumstances, the vinylidene potential surface will be bounded by the acetylene surface, permitting large excursions from the equilibrium geometry. The picture suggests the triplet levels may be perturbed by the large variations in the singlet structure and allow the occurrence of collision-induced quenching.

Lee and co-workers²² have extended theoretical models to include electronic quenching of small molecules. The model has been applied successfully to ${}^{1}SO_{2}$ fluorescence quenching. The model requires evaluation of several parameters which, in the case of triplet vinylidene, are not known. If a correlation was found, using estimates for the several parameters, it would be fortuitous and not likely to lead to greater insights into the quenching of triplet vinylidene in the absence of further experimental evidence.

Summary

Rate constants for collisional quenching of D_2CC (³B₂) by Ar, N₂, H₂, CO, and CH₄ have been measured for the first time, using vacuum-ultraviolet photolysis in conjunction with absorption spectroscopy techniques. Under our experimental conditions, no evidence of chemical quenching of vinylidene with these collision partners are observed.

A relatively good correlation between experimentally observed cross sections and the potential well depth model indicates that attractive forces may be significant in the quenching of excited vinylidene. These correlations are valuable in observing unusual behavior or in predicting nonreactive cross sections for additional gases.

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Pulse-Duration Effects on Competitive Reactions in Infrared Multiple-Photon Decomposition of CH₂CICHCIF and CHCIFCHCIF

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Vibrationally excited 1,2-dichlorofluoroethane and 1,2-dichloro-1,2-difluoroethane have been observed to dissociate competitively via two channels to form vibrationally excited HCl and HF. The fluence dependences of the branching ratio have been measured for both "short"-pulse (80-ns fwhm) and "long"-pulse (80-ns fwhm with $1-\mu$ s-fwhm tail) irradiations. The branching ratio shows not only fluence dependence but also pulse-duration dependence, that is, intensity dependence. When the reactant pressure is 1.0 Torr, collisional deactivation is expected to occur to a considerable extent under long-pulse irradiation while it can be ignored under short-pulse irradiation. The experimental results are interpreted by using the exact stochastic method based on the energy-grained master equations, which take into account collisional deactivation.

Introduction

The effects of laser intensity $(I, W \text{ cm}^{-2})$ and laser fluence $(\Phi, J \text{ cm}^{-2})$ on the dynamics of infrared multiple-photon excitation (IRMPE) and dissociation (IRMPD) have been extensively studied.¹ For many polyatomic molecules, the dissociation probability depends slightly on intensity but markedly on fluence

when collisions within the irradiation pulse duration can be ignored. For example, an increase of intensity by a factor of 200 has been observed to result in the increase of dissociation yield by only 30% in IRMPD of SF_{6} .² In such cases where the dissociation yield shows a fluence dependence, energy-grained master equations (EGME) have been shown to be valid to explain phenomenologically the mechanism of IRMPE and IRMPD³

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