

The ultraviolet photodissociation dynamics of 2-chloro-1,1-difluoroethylene

Yibo Huang^{a)} and Robert J. Gordon

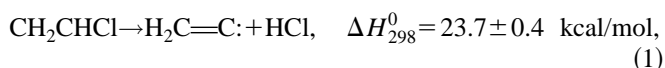
Department of Chemistry (m/c 111), University of Illinois at Chicago, 845 W. Taylor Street, Chicago, Illinois 60607

(Received 24 July 1996; accepted 15 October 1996)

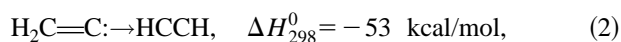
The rotational state distribution of HCl($v'=0$ and 1) produced in the 193 nm photodissociation of the title molecule was measured in a pulsed pump-and-probe experiment. The product state population was found to have a Boltzmann-like distribution, in agreement with a simple phase-space model. The photodissociation mechanism is proposed to be a three-center elimination of HCl to produce the $F_2C=C$: carbene. The barrier for rearrangement of this fragment is believed to be very large, so that any energy released in the eventual isomerization step does not affect the HCl state distribution. These results support our explanation of the nonstatistical state distribution of HCl produced in the photodissociation of vinyl chloride and dichloroethylene. © 1997 American Institute of Physics. [S0021-9606(97)01404-9]

The photodissociation dynamics of chlorinated ethylene molecules has been studied by kineticists for many years.^{1,2} The interest in this class of molecules stems in part from the possibility of their reacting simultaneously on more than one potential energy surface (PES). These molecules have a strong absorption band near 193 nm that corresponds to a $\pi \rightarrow \pi^*$ excitation of the double bond. The excited molecule can undergo a Woodward–Hoffman-forbidden, nonadiabatic surface crossing, resulting in the transfer of a nonbonding Cl electron to an antibonding orbital ($\pi, \pi^* \rightarrow n, \sigma^*$), leading to a prompt scission of a C–Cl bond.³ Alternatively, the molecule can undergo internal conversion to the ground PES, where C–Cl and C–H scission, as well as HCl and H₂ elimination, may occur.³ The branching ratios for these competing reaction paths and the disposal of available energy among the products provide a valuable test of our understanding of the effects nonadiabatic processes on the dynamics of energized molecules.

A number of recent studies provided detailed information regarding the translational and state distributions of various photofragments of this class of molecules.^{3–12} Experiments performed in this laboratory on vinyl chloride (VCl)^{3,5,6} showed that HCl is produced primarily by three-center elimination (3CE) on the ground PES,



resulting in a nonstatistical product state distribution. This mechanism is consistent with an *ab initio* PES calculation recently published by Riehl and Morokuma.¹³ To rationalize the HCl state distribution, we proposed that isomerization of vinylidene to form acetylene,



occurs before the fragments have completely separated, causing the products to recoil with excess energy. According to this mechanism, the first step determines the reaction path

(3CE vs 4CE) and the second step determines the energy disposal. In the absence of the isomerization step (or if isomerization occurs after the fragments have separated), the products are expected to have a statistical energy distribution, since the barrier for 3CE is expected to be small and the reaction path would have a loose transition state.

One way to test the proposed mechanism is to inhibit the isomerization step. This effect might be achieved, for example, by replacing the two hydrogen atoms attached to the β carbon by nonmigrating or slowly migrating groups. In this note we report such a test, using 2-chloro-1,1-difluoroethylene (CF_2CHCl , CFE) as the parent molecule.

Previous photochemical studies of CFE indicate that it is a promising molecule for such a study. The valence molecular orbitals of this molecule have the same configuration as VCl,¹⁴ namely $\cdots(a''[\pi_{Cl}])^2(a'[\sigma_{Cl}])^2(a''[\pi_{C=C}])^2$. Like VCl, it has a strong absorption at 193 nm, produced by a $\pi \rightarrow \pi^*$ transition. Reiser and Steinfeld¹⁵ found that HCl is a major photodissociation fragment. The only direct pathway for producing this fragment is 3CE,¹⁶



Despite the observation of HCl, no F_2C_2 was found among the products formed by infrared multiphoton excitation (IR-MPE). Using time-of-flight analysis, Sudbø, Schulz, Shen, and Lee,¹⁷ found that the translational energy distribution of HCl produced by IR-MPE could be fit with an RRKM model, in contrast to the case for most three- and four-center elimination reactions. These observations indicate that isomerization of the $F_2C=C$: carbene is at best a very slow process and should have no effect on the dynamics of the HCl elimination step. A measurement of the nascent rotational state distribution of HCl could, therefore, provide a test of our proposed reaction mechanism.

The experimental setup used in the present work was identical to that reported previously.^{3,5} Briefly, the experiment was performed in a pulsed molecular beam machine, using an ArF excimer laser (Lambda Physik EMG150) to photodissociate the parent molecule, and a frequency-doubled excimer-pumped dye laser (Lambda Physik

^{a)}Present address: Department of Chemistry, Notre Dame University, Notre Dame, IN 46556.

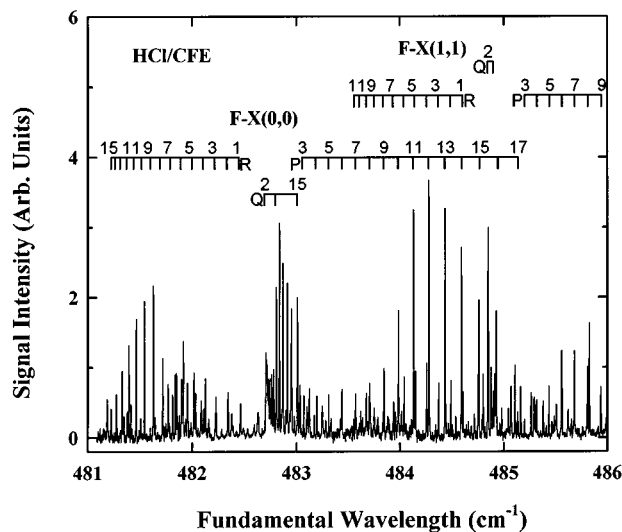


FIG. 1. (2+1) REMPI spectra of HCl obtained by 193 nm photodissociation of 2-chloro-1,1-difluoroethylene (CFE), showing rotationally resolved bands for the $v' = 0 \leftarrow v'' = 0$ and $v' = 1 \leftarrow v'' = 1$ vibrational transitions.

LPX200/FL3002) to probe the fragments. The molecular beam was generated by a pulsed valve (Newport BV-100V) fitted with a 0.5 mm orifice. The photolysis and probe lasers were counterpropagated perpendicular to the direction of the molecular beam. HCl was detected by 2+1 resonance-enhanced multiphoton ionization (REMPI), using the $F^1\Delta$ Rydberg state as the resonant intermediate level. The sample of CFE (PCR Research Chemicals Inc., 99.9%) was used as received without further purification, after transfer to a 500 ml Pyrex bulb.

Since the absorption cross section of CFE at 193 nm is only one sixth that of VCl, we were able to record only the 0,0 and 1,1 bands of the $F^1\Delta \leftarrow X^1\Sigma^+$ transitions, shown in Fig. 1. The short wavelength edge of the spectrum, at high rotational levels of the R-branch of the 0,0 transition (near 482 nm of the fundamental), may have some contamination resulting from photolysis by the probe laser, and accordingly was not used in our analysis. By measuring the background spectrum with the photolysis laser off, we verified that such contamination does not occur at longer wavelengths.

The rotational state populations for $\text{HCl}(v''=0)$ and 1) were extracted from the REMPI spectra, following the same procedure used in previous experiments to correct for the perturbation of the F state. The resulting state distributions are displayed in Fig. 2 in the form of Boltzmann plots. A least squares fit of the data to a Boltzmann distribution function gave rotational temperatures of 4200 ± 500 K for $\text{HCl}(v''=0)$ and 3400 ± 700 K for $\text{HCl}(v''=1)$. The observed populations may also be compared to a simple phase-space model, shown by the dashed curve in Fig. 2. These curves are the prior distribution functions, given by¹⁸

$$p^0(v, j, E_t | E_{\text{avl}}) \propto E_t^{1/2} \int_0^{E_{\text{avl}} - E_t} \rho_v(E_v) \times (E_{\text{avl}} - E_t - E_v)^{1/2} dE_v, \quad (4)$$

where $\rho_v(E_v)$ is the Whitten-Rabinovitch vibrational density of states,¹⁹ and $E_{\text{avl}} = 54$ kcal/mol is the available energy.

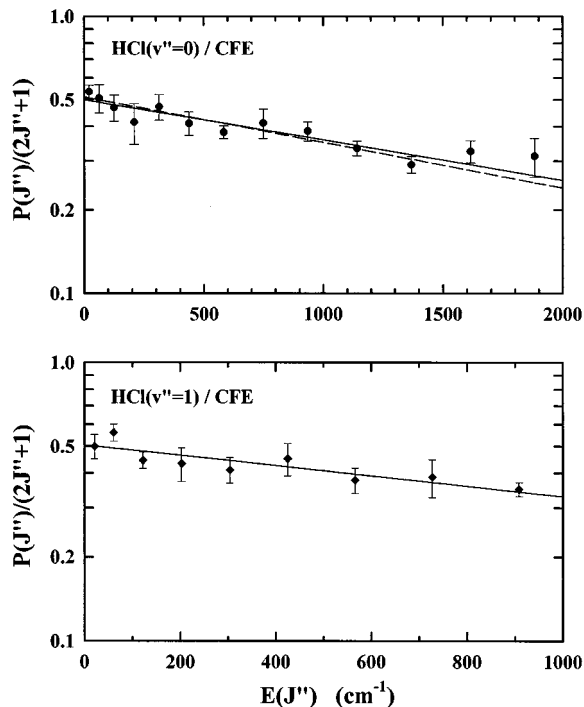


FIG. 2. Rotational state distributions of HCl obtained by photodissociating 2-chloro-1,1-difluoroethylene. The upper panel shows the populations of $\text{HCl}(v''=0)$, and the lower one shows those of $\text{HCl}(v''=1)$, both with arbitrary normalization. The solid lines are least-squares fits to Boltzmann distributions, giving rotational temperatures of 4200 ± 500 K for $v''=0$ and 3400 ± 700 K for $v''=1$. The dashed line in the upper panel is the phase-space calculation. For $\text{HCl}(v''=1)$ the slopes of the Boltzmann fit and the phase-space model were indistinguishable.

We see in Fig. 2 that within experimental error the rotational populations of HCl obtained from the photodissociation of CFE are in good agreement with the prior statistical distribution function for both $v''=0$ and 1. In our previous studies of VCl, partially deuterated VCl, and the three isomers of dichloroethylene (DCE), we found that the Boltzmann plots for $\text{HCl}(v''=0)$ had a bi-exponential form, while those for $\text{HCl}(v'' > 0)$ were Boltzmann-type but had rotational temperatures much higher than the prior values.

The differences between the rotational distributions of CFE and VCl may be understood in terms of the proposed reaction mechanism for VCl. According to the reaction path calculated by Morokuma,¹³ HCl is produced from VCl by 3CE, with a reverse barrier of approx 2.5 kcal/mole. The highly excited carbene then undergoes rapid (sub-ps) isomerization, with a forward barrier of 2–3 kcal/mole.^{20,21} Since the products at this point are still moving fairly slowly, a substantial fraction of the released energy is converted into both recoil and rotational energy of the fragments. This process is a concerted, asynchronous mechanism. In the case of CFE, replacing the remote hydrogen atoms by the heavier fluorine atoms changes the time scale for isomerization. The data of Reiser and Steinfeld¹⁵ imply that $\text{F}_2\text{C}=\text{C}:$ is a long-lived species, with essentially no rearrangement taking place to form perfluoroacetylene. A semiquantitative molecular orbit calculation predicted an activation barrier for the re-

arrangement reaction, $F_2C=C: \rightarrow FCCF$, that is, approx 60 kcal/mol greater than for the isomerization of vinylidene.²² Accordingly, elimination of HCl and isomerization of $F_2C=C:$ occur in a stepwise fashion, and any interaction between the fragments after they pass the critical configuration would be very weak. The biexponential rotational distribution of HCl($v''=0$) found for VCl and DCE was attributed to the small barrier encountered in the elimination step.³ It was conjectured that this barrier is reduced at higher v'' because of vibrational adiabaticity. In the case of CFE the most probable translational energy was found to be no greater than 0.1 kcal/mole,¹⁷ showing that energy released in the isomerization step (if it occurs at all) has no effect on the recoiling fragments. According to our mechanism, the absence of a reverse dissociation barrier should lead to a Boltzmann plot with a single rotational temperature, as observed.

Support by the Chemistry Division of the National Science Foundation is gratefully acknowledged.

¹M. J. Berry, *J. Chem. Phys.* **61**, 3114 (1974).

²M. Umemoto *et al.*, *J. Chem. Phys.* **83**, 1657 (1985).

³Y. Huang *et al.*, *J. Chem. Phys.* **103**, 5476 (1995).

⁴G. He *et al.*, *J. Chem. Phys.* **103**, 5476 (1995).

⁵P. T. A. Reilly, Y. Xie, and R. J. Gordon, *Chem. Phys. Lett.* **178**, 511 (1991).

⁶Y. Huang *et al.*, *J. Chem. Phys.* **99**, 2752 (1993).

⁷Y. Mo, K. Tonokura *et al.*, *J. Chem. Phys.* **97**, 4815 (1992).

⁸Y. Huang *et al.*, *Chem. Phys. Lett.* **229**, 621 (1994).

⁹G. He *et al.*, *J. Phys. Chem.* **97**, 2186 (1993).

¹⁰T. Suzuki *et al.*, *J. Phys. Chem.* **98**, 13447 (1994).

¹¹K. Sato *et al.*, *Chem. Phys. Lett.* **242**, 401 (1995); **245**, 432 (1995).

¹²D. J. Donaldson and R. Leone, *Chem. Phys. Lett.* **132**, 240 (1986).

¹³J. F. Riehl and K. Morokuma, *J. Chem. Phys.* **100**, 8976 (1994).

¹⁴A. W. Potts *et al.*, *Chem. Phys.* **115**, 253 (1987).

¹⁵C. Reiser and J. I. Steinfeld, *J. Phys. Chem.* **84**, 681 (1980).

¹⁶*JANAF Thermochemical Tables*, Natl. Bur. Stand. Ref. Data Ser. 37 [Natl. Bur. Stand., Washington, DC (1972)].

¹⁷Aa. Sudbó *et al.*, *J. Chem. Phys.* **69**, 2312 (1978).

¹⁸E. Zamir and R. D. Levine, *Chem. Phys.* **52**, 253 (1980).

¹⁹G. Z. Whitten and B. S. Rabinovitch, *J. Chem. Phys.* **38**, 2466 (1963).

²⁰M. M. Gallo, T. P. Hamilton, and H. F. Schaefer III, *J. Am. Chem. Soc.* **112**, 8714 (1990).

²¹K. M. Ervin, J. Ho, and W. C. Lineberger, *J. Chem. Phys.* **91**, 5974 (1990).

²²C. Hopkinson, M. Schoenborn, and I. G. Csizmaida, *Theor. Chim. Acta* **29**, 183 (1973).