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Rotational and vibrational energy distributions of HCl produced by three- and four-center eliminations of HCl from halogenated ethanes

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Abstract

Rotational and vibrational energy distributions of HCl from CF_3CClFH and $CClF_2CH_3$ have been measured using a $2+1$ resonantly enhanced multiphoton ionization (REMPI) technique. In the case of the three-center elimination from CF_3CClFH, the HCl products are rotationally and vibrationally cold. On the other hand, hot HCl products are produced in the case of the four-center elimination from $CClF_2CH_3$. The energy partitioning in the HCl eliminations has been discussed on the basis of structural change along the intrinsic reaction coordinate (IRC) or transition state structures obtained by ab initio molecular orbital (MO) calculations. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Elimination of HCl from chlorinated hydrocarbons is an important dissociation pathway in unimolecular dissociation of that in the ground electronic state [1]. Usually, the elimination of HCl occurs through three- or four-center transition states, depending on the molecular structure and the activation energies of both transition states.

Translational energy distributions released from the three- and four-center eliminations of HCl have been measured for several molecules using photofragment translational spectroscopy [2–5]. The exit barrier for the three-center elimination is generally much smaller than that for the four-center elimination, that is, typically a few tens of kJ/mol for the three-center elimination while 160–210 kJ/mol for the four-center elimination. In spite of this substantial difference, the average translational energy is not so much different between the three- and four-center eliminations of HCl from the saturated chlorinated hydrocarbons. This means that a smaller fraction of the exit barrier is converted to the relative translational energy of the products in the four-center elimination than in the three-center elimination, and that the internal energies of the products are expected to be larger for the four-center elimination than for the three-center elimination.

Several workers have studied internal state distributions of HCl produced by the elimination of HCl from several kinds of chloroethylenes following internal conversion from the initially prepared $\pi\pi^*$

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state to the ground state. Berry [6] measured vibronic state distributions of HCl from CH_2CHCl, CH_2CDCl, CH_2CCl_2, *cis*- and *trans*-CHClCHCl, and $CHClCCl_2$ using a chemical laser technique. He concluded that the distributions were non-statistical, and proposed a bootstrap reaction dynamic model to explain the non-statistical distributions. Donaldson and Leone [7] have measured the vibrational energy distributions of HCl from CH_2CHCl and *trans*-CHClCHCl using time-resolved FTIR emission spectroscopy. The measured distributions are in good agreement with Berry's distributions. However, they concluded that the distributions were statistical from the calculation with the HCl vibrational frequency at the transition state instead of that of free HCl. Gordon et al. [8] measured the rotational distributions of HCl from CH_2CHCl using a $2+1$ REMPI technique. The rotational distributions of $HCl(v''=1,2)$ were the Boltzmann-like distributions, while the distribution of $HCl(v''=0)$ consisted of two components with different rotational temperatures. Similar distributions were also observed for three isomers of dichloroethylene [9,10]. Several speculations have been done for the origin of these two different distributions: At first, Gordon and co-workers [8] proposed the possibility of the contributions of the three- and four-center eliminations of HCl. Later, they proposed another mechanism that the elimination of HCl was vibrationally adiabatic [11]. Sato et al. discussed the origin of the distributions on the basis of the competition of the three- and four-center eliminations. They suggested the importance of 1,2-shifts of H and Cl atoms for the elimination of HCl from 1,1-dichloroethylene [5,9]. A theoretical work supports that the 1,2-shifts of the H and Cl atoms are energetically possible for the three isomers of dichloroethylene [12]. These H and Cl atom migrations complicate the dissociation pathways for chloroethylenes, and make the understanding of the energy disposal to the products from the three- and four-center eliminations of HCl difficult.

In this Letter, the characteristics of the internal energy distributions of the HCl product are examined for the three- and four-center eliminations from 2-chloro-1,1,1,2-tetrafluoroethane (CTEFE) and 1-chloro-1,1-difluoroethane (CDFE), respectively. Compared with the elimination of HCl from chloroethylene, the chlorofluoroethane systems have an advantage for the determination of the transition state of the HCl elimination, because the isomerization of the molecules does not take place. We employed infrared multiphoton excitation (IRMPE) for preparing highly vibrationally excited molecules. The average excess energy above the transition state of the molecule excited by the IRMPE is generally small (80–130 kJ/mol). Therefore, employment of this excitation technique is advantageous for the elucidation of energy partitioning of exit barrier.

2. Experimental and ab initio calculation procedures

The experimental apparatus used in this work is the same as that in Ref. [13]. The CTEFE and CDFE molecules in supersonic molecular beams were dissociated at 9.294 and 10.504 μm, respectively, by a CO_2 laser (Lumonics TEA-840). The CO_2 laser light, the pulse shape of which was a 200 ns spike followed by a 2 μs tail, was focused with a ZnSe lens ($f = 30$ cm). The molecules were irradiated at 30, 430 and 1000 J/cm^2 of the laser fluence at the focus. The HCl product was probed by a $2+1$ REMPI technique combined with time-of-flight mass spectrometry. The rotational state distributions of HCl were determined by measuring the REMPI spectra of the two-photon $F\,^1\Delta(v', J') \leftarrow X\,^1\Sigma^+(v'', J'')$ transition [14,15]. The probe laser light was produced by frequency doubling of 480–505 nm light from a Nd:YAG Laser (Continuum Powerlight7010) pumped dye laser (Lambda Physik SCANMATE-2EY). The light was focused with a quartz lens ($f = 30$ cm). The output of the light was typically 1 mJ. The probe laser pulse, the duration of which was ~ 10 ns, was fired at 1.2 or 4.3 μs after the dissociation laser pulse.

In order for understanding the difference in dynamics between the three- and four-center eliminations, Ab initio MO calculations were done at the MP2(FC) level of theory. Wadt and Hay's effective core potentials [16] accompanied with split valence plus polarization functions (ECPDZP) were used as basis functions. All calculations were carried out using a Gaussian 92 program [17].

3. Results

3.1. Three-center HCl elimination from CTEFE

The IR multiphoton dissociation (IRMPD) of CTEFE was done at high (1010 J/cm^2) and low (30 J/cm^2) peak fluence. In Fig. 1 are shown REMPI spectra for HCl produced by the three-center elimination of HCl from CTEFE at the high fluence:

$$CF_3CHClF \rightarrow CF_3CF + HCl. \quad (1)$$

At the low fluence the REMPI spectrum of the (0, 1) and (1, 2) bands was not recorded because of low signal intensity. The rotational state distributions of HCl $P(E_{rot})$ are shown in Fig. 2. The $P(E_{rot})$'s were obtained from the measured rotational line intensities of the two-photon $F\,^1\Delta(v', J') \leftarrow X\,^1\Sigma^+(v'', J'')$ transition. Since the intensity loss of the rotational lines occurs in this transition, the line intensities of the measured spectra were corrected using experimental correction factors for the rotational line strength [15]. The relative population of HCl(v'' = 1, J'') was determined using the vibrational correction factor [18] for the sensitivity difference between (1, 1) and (0, 0) band. Since the vibrational correction factor for the (1, 2) band has not been reported, the relative population of HCl(v'' = 2, J'') was simply determined by scaling the rotational line intensities of the (1, 2) band with the average ratio of the rotational line intensities of the (1, 1) band to those of the (0, 1) band and with the ratio of the Franck–

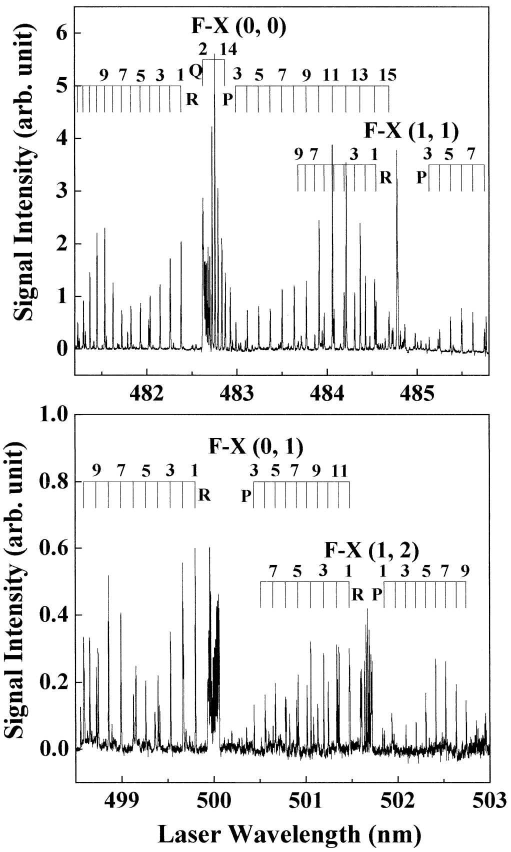

Fig. 1. Intensity corrected REMPI spectrum of HCl from CF_3CHClF at high fluence.

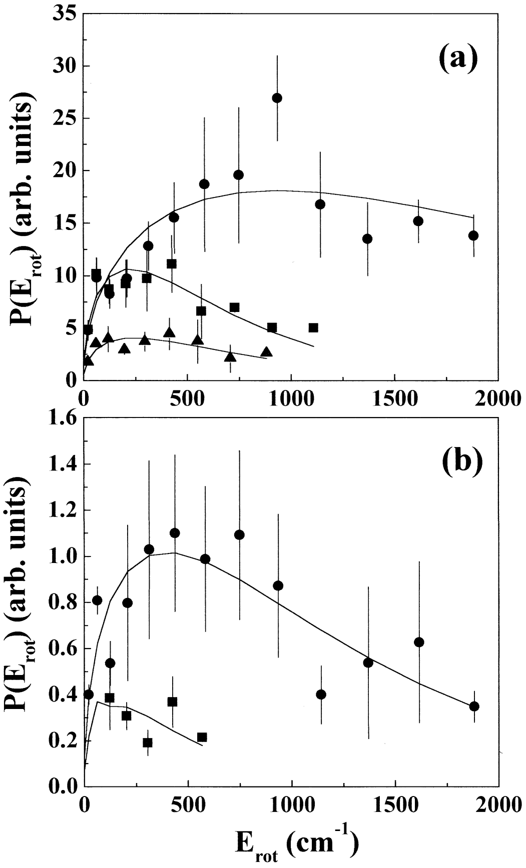

Fig. 2. Rotational energy distributions of HCl from CF_3CHClF at (a) high and (b) low fluences; (●) v'' = 0, (■) v'' = 1, and (▲) v'' = 2. The solid lines indicate the best fits to the Boltzmann distribution.

Table 1
Average rotational energies $\langle E_{\mathrm{rot}} \rangle$ of HCl produced by the three-center HCl elimination from CF_3CHClF

v	$\langle E_{\mathrm{rot}} \rangle$ (kJ/mol)	
	high fluence	low fluence
0	23 ± 5	9 ± 2
1	5.4 ± 0.8	6 ± 2
2	5.9 ± 0.8	–

Condon factor for the (0, 1) band to that for the (1, 2) band. The solid lines in Fig. 2 indicate the best fits to the Boltzmann distributions. The average rotational energies at the high and low fluences are listed in Table 1. The relative populations of the vibrational levels obtained by the integration of the rotational distributions are $1.0 : 0.29 \pm 0.12 : 0.12 \pm 0.05$ for $v'' = 0 : v'' = 1 : v'' = 2$ at high CO_2 laser fluence and $1.0 : 0.52 \pm 0.32$ for $v'' = 0 : v'' = 1$ at low fluence.

3.2. Four-center HCl elimination from CDFE

The IRMPD of CDFE was done at peak fluence of 430 J/cm^2. Fig. 3 shows the REMPI spectrum of HCl produced by four-center elimination of HCl from CDFE:

$$CClF_2CH_3 \rightarrow CF_2{=}CH_2 + HCl. \qquad (2)$$

The $P(E_{\mathrm{rot}})$'s are shown in Fig. 4. Only the $P(E_{\mathrm{rot}})$ for $v'' = 2$ can be well fitted to a Boltzmann distribution with an average energy of 5.4 ± 1.4 kJ/mol as shown in Fig. 4. The fit of the $P(E_{\mathrm{rot}})$ for $v'' = 1$ to a Boltzmann distribution is poor, and the $P(E_{\mathrm{rot}})$ for $v'' = 0$ could not be fitted to a Boltzmann distribution. Since all $P(E_{\mathrm{rot}})$'s increase with the rotational energy in the range of the measured rotational lines, the relative populations of the vibrational levels could not be calculated by summing up the relative populations of all significant rotational levels. The average relative population ratio of HCl at different vibrational states by summing up the relative populations over all measured rotational levels is $1.0{:}4.5 \pm 1.3{:}92 \pm 26$ for $v'' = 0{:}v'' = 1{:}v'' = 2$. Therefore, the yields of each vibrational state of HCl should be $v'' = 0 < v'' = 1 < v'' = 2$.

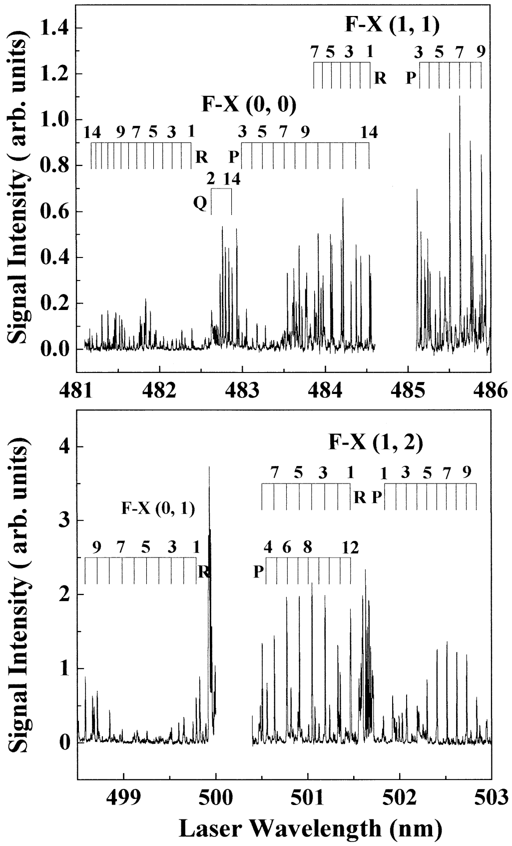

Fig. 3. Intensity corrected REMPI spectrum of HCl from $CClF_2CH_3$.

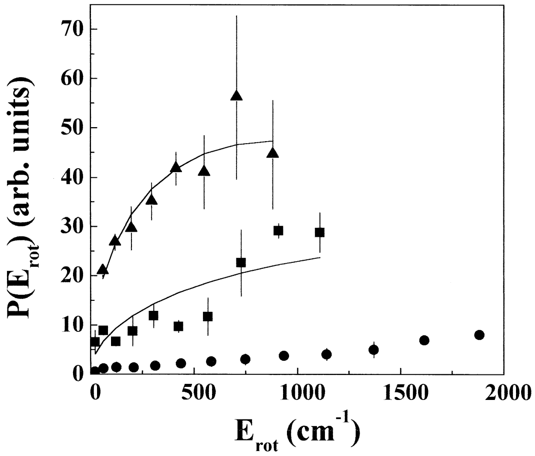

Fig. 4. Rotational energy distributions of HCl from $CClF_2CH_3$; (●) $v'' = 0$, (■) $v'' = 1$, and (▲) $v'' = 2$. The solid lines indicate the best fits to the Boltzmann distribution.

4. Discussion

The internal state distributions of HCl are remarkably different for the three- and four-center elimination reactions studied in this work. In the case of the three-center elimination of HCl from CTEFE, the $P(E_{\mathrm{rot}})$'s for $v''=0$ to 2 are well reproduced by Boltzmann distributions, and the vibrational populations are $v''=0>v''=1>v''=2$. On the other hand, in the case of the four-center elimination from CDFE, the $P(E_{\mathrm{rot}})$'s for $v''=0$ and 1 could not be fitted to a Boltzmann distribution, and the vibrational populations are $v''=0<v''=1<v''=2$.

In the case of the three-center HCl elimination, the exit barrier is small: For the elimination from CTEFE, the exit barrier was estimated to be ~16 kJ/mol from the product translational energy distribution [3]. Moreover, most of the barrier energy is released as translation [2,3]. Thus, the internal energy of HCl comes mainly from excess energy above the exit barrier. A small conversion fraction of the exit barrier to the vibrational states of HCl should indicate that the HCl and CF_3CF are almost formed at the transition state. In fact, the H–Cl distance at the transition state is calculated to be 1.38 Å, which is only 0.11 Å longer than the normal HCl in contrast with the H–Cl distance (1.77 Å) of HCl produced by the four-center elimination.

The average rotational energy in the $v''=0$ state decreases with decreasing laser fluence. This behavior is explained by the change of the average excess energy. In an IRMPE the average excitation energy of a molecule before dissociation is determined by the competition of the excitation process to upper vibrational levels above the dissociation limit with the dissociation process. The excitation rate is proportional to laser intensity, which is proportional to laser fluence if the laser pulse width is constant in such case as this experiment. Therefore, the average excess energy is expected to be higher at higher fluence.

In the case of four-center elimination, the exit barrier, which is typically 160–210 kJ/mol, is much higher than that for the three-center elimination, and only 20–30% of the exit barrier is released as the relative translational energy. In the HCl elimination from CDFE, the average relative translational energy (50 kJ/mol) is only 27% of the exit barrier (184 kJ/mol)[1]. Therefore, most of the exit barrier is released as the internal energy of the HCl and CH_2CF_2 fragments. Since the population of the HCl at the vibrational state higher than $v''=2$ could not be determined in this study, the average vibrational energy of HCl cannot be deduced. The average vibrational energy, however, is expected to be at least 67 kJ/mol, because the vibrational population of HCl($v''=2$) should be much larger than HCl($v''=0,1$). Statistical partitioning of the exit barrier to all degrees of freedom of the fragments results in the monotonically decreasing vibrational populations with increasing vibrational quantum numbers. The average vibrational energy of HCl with the statistical vibrational distribution is 6.3 kJ/mol. Even if we use the vibrational frequency of HCl at the transition state according to Donaldson and Leone's analysis [7], the average energy is only 22 kJ/mol. Therefore, the observed vibrational distribution indicates that the energy partitioning to HCl is non-statistical for the four-center elimination of HCl, and more energies are partitioned to HCl vibration.

The favorable partitioning of the exit barrier to HCl vibration is due to dynamics beyond the transition state and can be qualitatively explained by structural change along IRC shown in Fig. 5, where the length along IRC is represented by s. The H–Cl distance drastically changes from 1.77 Å at $s=0$ to 1.35 Å at $s=0.9$ with the potential energy decrease of 80.4 kJ/mol in early stage of reaction. Since other coordinates such as the distance between the center-of-masses of HCl and CH_2CF_2 and the C–C distance change less than the H–Cl distance in this stage, the potential energy released in this stage is expected to be converted mainly to HCl vibration. Kato and Morokuma [22] did an IRC analysis more quantitatively for four-center elimination of HF from CH_3CH_2F. In their calculation, the potential energy

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[1] The exit barrier is calculated using the heat of formation of CH_3CClF_2 (−529.7 kJ/mol [19]), that of CH_2CF_2 (−335 kJ/mol [20]), that of HCl (−92 kJ/mol [20]), and the activation energy (289 kJ/mol [21]). Sudbø et al. [2] calculated to be 230 kJ/mol by taking the heat of formation of CH_3CClF_2 to be −490 kJ/mol, which was obtained by the additivity rule. The exit barrier (162 kJ/mol) obtained using an ab initio MO method at MP2/ECPDZP level of theory supports our estimation using the experimental heat of formation of CH_3CClF_2 cited in Ref. [19].

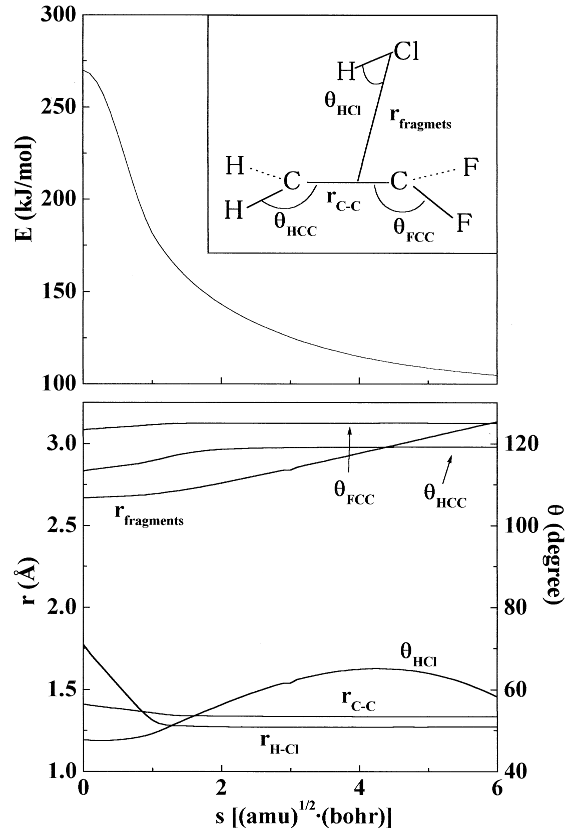

Fig. 5. Energy and structural change of $CClF_2CH_3$ along IRC (s). The insertion in the upper figure indicate the definition of structural parameters.

released from $s = 0$ to $s = 0.5$ is converted to kinetic energy along the IRC and energy transfer between IRC and the HF vibration takes place in the early stage ($0.5 < s < 0.83$). They estimated that two-thirds of the IRC energy is converted to the HF vibration in this region. If we assume that the energy transfer between IRC and the HCl vibration is similar to the case of the HF elimination, the HCl vibrational energy amounts to ~ 53.6 kJ/mol. If we consider the difference between the experimental (184 kJ/mol) and calculated (162 kJ/mol) exit barrier, the estimated HCl vibrational energy becomes ~ 61 kJ/mol. Although this estimation is rough, it can be explained qualitatively that high vibrational excitation in HCl occurs during dissociation, and this is in good agreement with the present experimental results.

The comparison of $P(E_{\mathrm{rot}})$'s for the four-center elimination with that for the three-center elimination shows that HCl produced by the four-center elimination is rotationally excited more than that produced by the three-center elimination. The angle θ between the H–Cl bond and the line joining the center-of-masses of HCl and CH_3CClF_2 changes at $s \leq 0.9$ as shown in Fig. 5. This change will produce torque and give rotationally excited HCl molecules.

5. Conclusions

The rotational and vibrational energy distributions of HCl produced by the four- and three-center eliminations were measured. The distributions are remarkably different in two types of reactions: In the case of the four-center elimination, the vibration and rotation of HCl is excited significantly as a result of dynamical effect during dissociation. This can be explained on the basis of the structural change along IRC beyond the transition state. On the other hand, in the case of the three-center elimination, the vibrational and rotational distributions are statistical, and most of energy comes from the excess energy above the transition state. This is because the exit barrier is small and because the C–Cl distance is small at the transition state.

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