

Vacuum-Ultraviolet Spectral Studies of Several Chlorofluoroethylenes

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Abstract: The vacuum-ultraviolet spectra are reported for three chlorofluoroethylenes in the region 2100–1200 Å. The spectral quantities assigned are the $V \leftarrow N$ ($\pi^* \leftarrow \pi$) transition energies and the energies of bands belonging to ns , np , and nd Rydberg series which converge on the π ionization energies. The ionization energies of the three molecules are 9.97 eV for 1-chloro-1-fluoroethylene, 9.76 eV for 2-chloro-1,1-difluoroethylene, and 9.76 eV for chlorotrifluoroethylene. Apparent effects exerted by substitution of the halogens, fluorine and chlorine, on the π and π^* orbital energies are described through comparison of the data for these three molecules and other halogen-substituted ethylenes. An empirical method for calculating π and π^* orbital energies is presented. Results are in good agreement with the observed data, and predictions are made for several chlorofluoroethylenes not yet studied.

Vacuum-ultraviolet absorption spectra of the chloroethylenes^{1–5} and the fluoroethylenes⁶ disclose several similarities in the spectral effects of substitution of chlorine and fluorine at the olefinic double bond. In an effort better to understand substituent effects, particularly on the π and π^* orbital energies of ethylene, the vacuum-ultraviolet absorption spectra for several chlorofluoroethylenes have been obtained and are considered here. For this study it was necessary to obtain two spectral quantities: (1) the energy of the $V \leftarrow N$ ($\pi^* \leftarrow \pi$) transition, and (2) the ionization energy of the π electron.

Experimental Section

The spectra were measured on a McPherson Model 225 monochromator with a 1-m concave grating having 600 lines/mm. A double-beam attachment was used, and the spectra were recorded photoelectrically. The light source was a Hinteregger hydrogen discharge lamp. The sample was placed in a 10-cm stainless-steel cell with lithium fluoride windows and pressure readings were made with a CEC "autovac" gauge, which had been calibrated over the range with a McLeod gauge. Samples were introduced at room temperature in the vapor state at pressures of 0.1 Torr. Higher pressures were used to enhance weak bands.

The samples were obtained from Peninsular Chemresearch and were purified by low-temperature vacuum distillation. The distillation manifold was connected directly to the sample cell and the sample was introduced through a stainless-steel Nupro valve. The CEC "autovac" gauge head was connected to the sample chamber between the Nupro valve and the sample chamber. The mercury in the McLeod gauge was exposed to the system only for the time required for calibration of the CEC gauge, and the samples actually used for the spectral work were never in contact with the mercury.

Results

The spectra of three chlorofluoroethylenes, 1-chloro-1-fluoroethylene (FCIC_2H_2), 2-chloro-1,1-difluoroethylene ($\text{F}_2\text{C}_2\text{ClH}$), and chlorotrifluoroethylene ($\text{F}_2\text{C}_2\text{FCl}$), are presented in Figures 1–3. The spectrum of another molecule, 1,1-dichloro-2,2-difluoroethylene ($\text{F}_2\text{C}_2\text{Cl}_2$),

has been presented in an earlier work.⁷ Spectral assignments for the chlorofluoroethylenes investigated are given in this section.

Basically two factors influenced the assignments of the bands in Table I to the $V \leftarrow N$ ($\pi^* \leftarrow \pi$) transi-

Table I. $V \leftarrow N$ Absorption Band with Vibrational Components (cm^{-1})

ν_{obsd}	$\Delta\nu$ (vib spacing)	
1-Chloro-1-fluoroethylene		
56,561 ^a	539	
57,100		1326
57,887	524	
58,411		1362
59,249	524	
59,773		1357
60,606		
2-Chloro-1,1-difluoroethylene		
56,379	1501	
57,880 ^a	1513	
59,393		
Chlorotrifluoroethylene		
59,787	309	
60,096		1524
61,312	291	
61,603		1522
62,834 ^a	305	
63,139		1533
64,367		1535
65,902		1483
67,385		

^a Band maximum.

tion. The factors are (1) the similarities in position, shape, and intensity among the bands assigned here and those reported previously for other substituted ethylenes and (2) the vibrational structure of the excited state. This excited state has a $\text{C}=\text{C}$ stretching frequency which is lower than that of the Rydberg states of the same molecule.

The ground-state $\text{C}=\text{C}$ stretching frequencies are as follows: for FCIC_2H_2 ,⁸ 1656; $\text{F}_2\text{C}_2\text{ClH}$,⁹ 1745; and for $\text{F}_2\text{C}_2\text{ClF}$,¹⁰ 1802 cm^{-1} . In all three systems

- (1) A. D. Walsh, *Trans. Faraday Soc.*, **41**, 35 (1945).
- (2) A. D. Walsh, P. A. Warsop, and J. A. B. Whiteside, *ibid.*, **64**, 1432 (1968).
- (3) C. M. Humphries, A. D. Walsh, and P. A. Warsop, *ibid.*, **63**, 513 (1967).
- (4) R. Bralsford, P. V. Harris, and W. C. Price, *Proc. Roy. Soc., Ser. A*, **258**, 459 (1960).
- (5) J. P. Teegan and A. D. Walsh, *Trans. Faraday Soc.*, **47**, 1 (1951).
- (6) G. Belanger and C. Sandorfy, *J. Chem. Phys.*, **55**, 2055 (1971).

- (7) J. D. Scott and B. R. Russell, *Chem. Phys. Lett.*, **9**, 375 (1971).
- (8) J. R. Nielsen and J. C. Albright, *J. Chem. Phys.*, **26**, 1566 (1957).
- (9) J. R. Nielsen and C. Y. Liang, *ibid.*, **20**, 1090 (1952).
- (10) D. E. Mann, N. Aquista, and E. K. Plyler, *ibid.*, **21**, 1949 (1953).

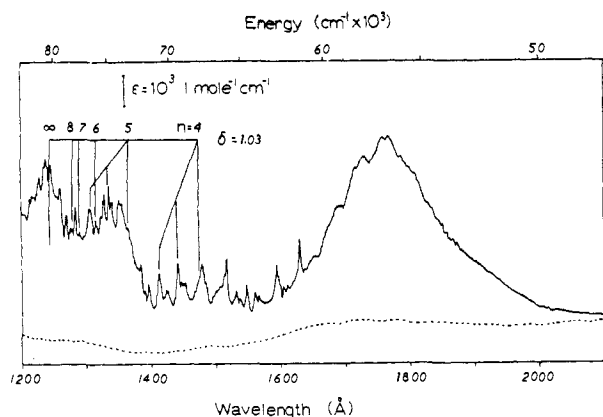


Figure 1. Absorption spectrum of 1-chloro-1-fluoroethylene (dashed line is base line).

(Table I) there are vibrational spacings corresponding to energies somewhat lower than the respective ground-state C=C stretching frequencies. To the red of the 1768-Å member of FCIC_2H_2 is diffuse structure belonging to two lower energy members of the progression. In addition to the C=C stretching progressions in FCIC_2H_2 and $\text{F}_2\text{C}_2\text{ClF}$, lower energy vibrational spacings are also observed. The *ca.* 530- cm^{-1} spacing in FCIC_2H_2 is tentatively assigned as the excited-state C-Cl stretching frequency and the *ca.* 300- cm^{-1} spacing in $\text{F}_2\text{C}_2\text{ClF}$ is assigned as the excited-state F-C-Cl angle-deformation frequency. No vibrational structure appears in the $V \leftarrow N$ transition of $\text{F}_2\text{C}_2\text{Cl}_2$. For the purpose of discussion, the $V \leftarrow N$ band maximum will be considered as the energy of the transition. This transition in $\text{F}_2\text{C}_2\text{Cl}_2$ is 57,470 cm^{-1} .

Many of the remaining bands were found to fit Rydberg progressions of the form

$$\nu_n(\text{cm}^{-1}) = \text{IP}(\text{cm}^{-1}) - R(\text{cm}^{-1})/(n - \delta)^2$$

where n is the principal quantum number of the excited state and δ is the quantum defect number, having a value around 1.0 for ns Rydberg states, 0.5 for np Rydberg states, and 0.1 for nd Rydberg states.¹¹ The values of δ have been considered to be constant.

The Rydberg series are given in Table II. The ns Rydberg series are present in all systems including $\text{F}_2\text{C}_2\text{Cl}_2$,⁷ and the limits of these series are considered to be the π ionization potentials in the discussion to follow. The vibrational series which join to members of the Rydberg progressions are given in Table II. Both the 4s and 5s members of all three systems contain the C=C stretching frequencies reduced relative to the ground states. The reductions are smaller than those observed for the appropriate excited states. A second vibration of *ca.* 350 cm^{-1} appears in the 5s member of FCIC_2H_2 and a third vibration of *ca.* 200 cm^{-1} appears on every C=C stretching member and also appears on two of the 350- cm^{-1} members. The 350- and 200- cm^{-1} frequencies in FCIC_2H_2 are assigned to the F-C-Cl bending modes of the 5s Rydberg excited state. The ground-state frequencies are 433 and 370 cm^{-1} .⁸ The nd progression of $\text{F}_2\text{C}_2\text{ClF}$ and the np progression of $\text{F}_2\text{C}_2\text{ClH}$ also reveal the C=C stretching frequencies. At this point, a note should be

(11) G. Herzberg, "Electronic Spectra of Polyatomic Molecules," Van Nostrand, Princeton, N. J., 1967.

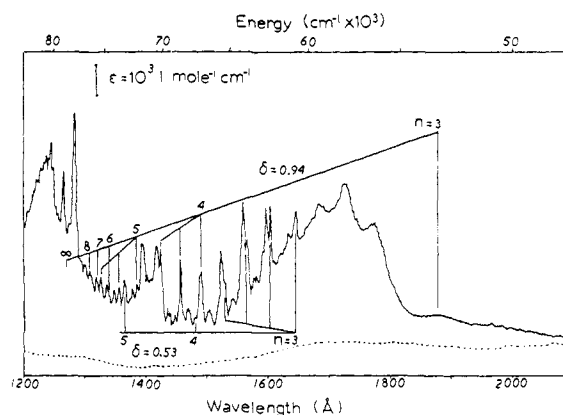


Figure 2. Absorption spectrum of 2-chloro-1,1-difluoroethylene.

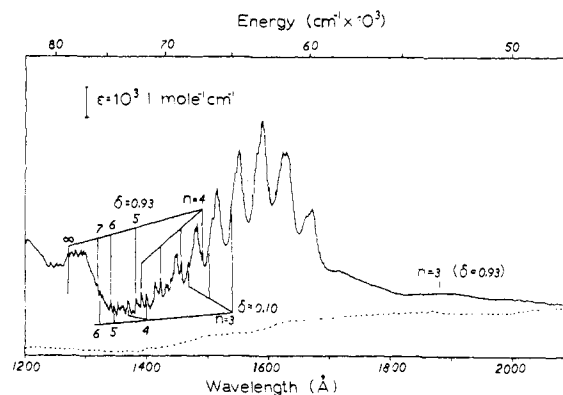


Figure 3. Absorption spectrum of chlorotrifluoroethylene.

added concerning the 3s member assigned for FCIC_2H_2 . The band assigned to this transition is the tail on the low-energy side of the $V \leftarrow N$ transition. This asymmetry appears to be centered at *ca.* 1900 Å.

Comparison of the Rydberg data with the photoelectron spectra of $\text{F}_2\text{C}_2\text{ClH}$, $\text{F}_2\text{C}_2\text{ClF}$, and $\text{F}_2\text{C}_2\text{Cl}_2$ reported by Lake and Thompson¹² resulted in several interesting observations. First, a comparison of the π ionization energies from the photoelectron (PE) spectra with the ns series limits (S) reveals the following agreement: 9.84 (PE) and 9.76 eV (S) for $\text{F}_2\text{C}_2\text{ClH}$, 9.84 (PE) and 9.76 eV (S) for $\text{F}_2\text{C}_2\text{ClF}$, and 9.65 (PE) and 9.69 eV (S) for $\text{F}_2\text{C}_2\text{Cl}_2$. The photoelectron spectra revealed C=C vibrational structure on the bands assigned to the π ionization energies for all three molecules. The average values reported for these frequencies in the ions are 1570 cm^{-1} for $\text{F}_2\text{C}_2\text{ClH}$, 1610 cm^{-1} for $\text{F}_2\text{C}_2\text{ClF}$, and 1500 cm^{-1} for $\text{F}_2\text{C}_2\text{Cl}_2$. The C=C stretching frequencies of the ns Rydberg states are almost identical with that of the respective ion. A correspondence was observed between the relative intensities of the C=C vibrational members in both the photoelectron and the ns Rydberg bands. In all three molecules reported by Lake and Thompson, the members of maximum intensity in the ionization bands were the same as observed in the ns absorption bands. The above observations suggest that the geometries of the molecules in the lower Rydberg states are close to those of the ions.

(12) R. F. Lake and H. Thompson, *Proc. Roy. Soc., Ser. A*, **315**, 323 (1970).

Table II. Rydberg Progressions (cm⁻¹)

<i>n</i>	ν_{enld}	ν_{obsd}	$\Delta\nu$ (vib spacing)
1-Chloro-1-fluoroethylene			
<i>ns</i> Series, $\delta = 1.03$			
3	52,124	52,500	
4	67,959	67,800	1447
		69,247	1454
		70,701	
5	73,437	73,465	205
		73,670	
		73,833	368
		74,923	1458
		75,120	197
		75,273	350
		75,460	187
		76,353	1430
		76,552	199
		76,693	340
		76,870	177
6	75,957	75,976	
7	77,321	77,298	
8	78,141	78,143	
∞	80,400		
2-Chloro-1,1-difluoroethylene			
<i>ns</i> Series, $\delta = 0.94$			
3	52,881	53,200	
4	67,020	67,002	1562
		68,564	1567
		70,131	
5	72,083	72,103	1573
		73,676	1557
		75,233	
6	74,454	74,477	
7	75,752	Hidden	
8	76,538	76,529	
∞	78,740		
<i>np</i> Series, $\delta = 0.53$			
3	60,538	60,728	1558
		62,286	1542
		63,828	1544
		65,372	
4	67,436	67,431	1577
		69,008	
5	73,058	73,062	
∞	78,550		
Chlorotrifluoroethylene			
<i>ns</i> Series, $\delta = 0.93$			
3	53,375	53,191	
4	67,172	67,024	1610
		68,634	1601
		70,235	1599
		71,834	
5	72,148	72,254	1596
		73,850	1593
		75,443	
6	74,488	74,500	
7	75,777	75,758	
8	76,551	76,587	
∞	78,740		
<i>nd</i> Series, $\delta = 0.10$			
3	65,604	64,956	1574
		66,530	1544
		69,074	
4	71,437	71,398	1568
		72,966	
5	74,082	74,140	
6	75,500	75,466	
∞	78,652		

In two of the spectra (FCIC₂H₂ and F₂C₂ClH), intense bands originate between 1600 and 1650 Å. Both bands have vibrational structure with energy spacings corresponding to the C=C stretching frequency (see Table III for a tabulation of these two bands). Two

Table III. Other Vibrational Progressions

ν_{obsd}	$\Delta\nu$ (vib spacings)
2-Chloro-1,1-difluoroethylene	
62,555	1519
64,074	1508
65,582	1546
67,128	
1-Chloro-1-fluoroethylene	
61,276	1374
62,641	1343
63,984	

possible assignments have been considered for these bands, (1) $3p \leftarrow \pi$ and (2) $\pi^* \leftarrow n\pi$ transition, where the $n\pi$ orbital is the chlorine nonbonding $3p$ orbital which conjugates with the π framework. The choice of the latter possibility is favored because the $\pi^* \leftarrow n\pi$ is an allowed transition and would be expected to occur at higher energy than the $V \leftarrow N$ transition (the $n\pi$ ionization potential is about 2 eV higher than that of the π orbital).¹²

Other transitions, more atomic in nature, are expected from excitation of the chlorine $3p$ nonbonding electrons to excited orbitals localized on the chlorine atom. These transitions have been observed in all of the chloroethylenes,¹⁻⁵ and the bands are quite similar to those in the spectra of the chlorofluoroethylenes. The intense band centered at *ca.* 1400 Å in F₂C₂ClH is tentatively assigned to the $4s \leftarrow 3p$ "atomic" transition, where this $4s$ orbital is localized on the chlorine atoms and is not the $4s$ molecular Rydberg orbital discussed earlier. The analogous transitions in FCIC₂H₂ and F₂C₂ClF are expected to be shifted to higher energies because of the presence of the geminal fluorine. The absorptions at *ca.* 1350 Å in FCIC₂H₂ and *ca.* 1300 Å in F₂C₂ClF can be attributed, at least partly, to the $4s \leftarrow 3p$ transition. The intense bands at higher energies correspond to higher chlorine atomic Rydbergs as assigned in the chloroethylenes. In the 1450–1620-Å region, several bands have not been assigned for FCIC₂H and F₂C₂ClH.

Discussion

The discussion is presented in terms of a totally empirical comparison of the chloro- and fluoroethylenes to the chlorofluoroethylenes with respect to halogen substituent effect on the π and π^* orbital energies. For the purpose of this discussion three assumptions have been made. (1) The ground-state geometries of the molecules are planar. (2) The energy of the π C=C bonding orbital is represented by the spectrally determined ionization energy of the π electron. The energies of the bound electrons are considered to be negative in sign; therefore, the π energy of a system is simply the negative of the ionization potential (*ns* series limit). (3) The energy of the π^* C=C antibonding orbital is above that of the π orbital by an amount equal to the $V \leftarrow N$ transition energy.

Evaluations of the π and π^* energies, according to these assumptions, were made for the chloroethylenes and the fluoroethylenes and are listed in Table IV.

Several effects or perturbation-type parameters were determined from the experimental data given in Table IV. The parameters are defined as the energies which

Table IV. π and π^* Energies (cm^{-1}) of the Chloro- and Fluoroethylenes

Molecule	$-\pi$ energy		$-\pi^*$ energy	
	X = F ^a	X = Cl	X = F ^a	X = Cl
X ₂ C ₂ X ₂	81,624	75,276 ^b	9,944	24,576 ^d
X ₂ C ₂ XH	81,867	76,220 ^c	19,367	25,200 ^d
X ₂ C ₂ H ₂	83,076	79,526 ^e	22,466	26,726 ^f
<i>cis</i> -XHC ₂ XH	82,673	77,937 ^d	19,637	25,305 ^d
<i>trans</i> -XHC ₂ XH	82,109	77,680 ^c	23,355	26,390 ^d
XHC ₂ H ₂	83,560	80,700 ^d	23,500	26,650 ^d
H ₂ C ₂ H ₂	84,750 ^g		23,020	

^a See ref 6. ^b See ref 3. ^c Photoionization data (see ref 4).
^d See ref 1. ^e See ref 2. ^f See ref 5. ^g W. C. Price and W. T. Tutte, *Proc. Roy. Soc., Ser. A*, **174**, 207 (1940).

must be added to the π and π^* orbital energies of a parent molecule to obtain the corresponding energies of the substituted molecule formed by halogen (fluorine or chlorine) monosubstitution. This parameter is the value obtained by subtraction of the particular orbital energy of the parent molecule from the corresponding energy of the substituted molecule. The resulting parameters were determined from the chloroethylenes and the fluoroethylenes and are given in Table V. The parent compound of each substituted

Table V. Perturbation Parameters (cm^{-1})

Molecule	<i>i</i>	π parameters		π^* parameters	
		F _{<i>i</i>}	Cl _{<i>i</i>}	F _{<i>i</i>'}	Cl _{<i>i</i>'}
X*HC ₂ H ₂	1	1190	4150	-480	-3630
X*XC ₂ H ₂	2	484	1174	1034	-76
<i>cis</i> -X*HC ₂ XH	3	887	2763	3863	1345
<i>trans</i> -X*HC ₂ XH	4	1451	3020	145	260
<i>cis</i> -X*XC ₂ XH	5	242	1460	3988	1190
<i>trans</i> -X*XC ₂ XH	6	806	1717	270	105
X ₂ C ₂ X*H	7	1209	3306	3099	1526
X*XC ₂ X ₂	8	243	944	9423	624

molecule in Table V can be found by removal of the halogen (X*) marked with an asterisk and by subsequent substitution of a hydrogen atom in that position. The representation of the parameters for the fluorine or chlorine are F_{*i*} or Cl_{*i*} and F_{*i*'} or Cl_{*i*'} for the effects on the π and π^* energies, respectively (the subscripts are only for reference).

The use of the parameters involved the "construction" of the substituted molecules from ethylene, one halogen at a time. These parameters correspond to all possible chlorine and fluorine substitutions when the halogens in the parent molecule are the same as the substituent. For the chlorofluoroethylenes there are two kinds of halogens; nevertheless, these parameters are used and the particular value is determined by the geometrical relationship between the position of the substituent and other halogens in the parent molecule. Since all of the molecules are "constructed" from ethylene, the appropriate X_{*i*} parameter is added to the π energy of ethylene corresponding to the first substitution. The resulting molecule is now the parent for the next substitution and the energy resulting from the addition of X_{*i*} to the π energy of ethylene is the π energy of the parent. The subsequent substitutions involve the addition of the appropriate X_{*i*}'s (F_{*i*} or Cl_{*i*}), where the values of *i* depend on the kind of halogen substituted and the position. The process is repeated until all

substitutions have been made. Calculation of the π^* energy is analogous to the π energy evaluation, except that the initial parent energy is the π^* energy of ethylene and the parameters are the X_{*i*} values.

The order of the substitutions for a particular "construction" is arbitrary; therefore, several different energies can be calculated for each of the chlorofluoroethylenes. Using as an example the "construction" of F₂C₂ClF with the chlorine substitution considered first, followed by the three fluorines, the evaluation of the π energy is: π energy of F₂C₂ClF = π energy of H₂C₂H₂ + Cl₁ + F₂ + F₇ + F₈ = -78,764 cm^{-1} . The experimental value is -78,740 cm^{-1} ; therefore, this particular order of substitution results in a value which agrees quite well with the experimental energy.

For all of the molecules given in Table VI, very good agreement was found to exist between the experimental and calculated π energies when the latter were evaluated by considering substitution of the chlorine(s) first followed by the fluorine(s). Similar calculations were

Table VI. Observed and Calculated π and π^* Orbital Energies (cm^{-1}) of the Chlorofluoroethylenes

Molecule	$-\pi$ energy		$-\pi^*$ energy	
	Calcd ^a	Obsd	Calcd ^b	Obsd
FCIC ₂ H ₂	80,216	80,420	23,576	23,859
F ₂ C ₂ ClH	79,007	78,740	20,940	20,860
F ₂ C ₂ ClF	78,764	78,740	18,743	15,846
			(13,094) ^a	
F ₂ C ₂ Cl ₂	77,804	78,074	20,316	20,682
<i>cis</i> -HCIC ₂ FH	79,813	79,500	22,155	
<i>trans</i> -HCIC ₂ FH	79,247	79,600	23,240	
<i>cis</i> -FCIC ₂ HF	79,055	79,500	19,532	
<i>trans</i> -FCIC ₂ HF	79,055	79,300	22,165	
FCIC ₂ Cl ₂	75,977		21,426	

^a Perturbation by chlorine(s) first followed by fluorine(s). ^b Perturbation by fluorine(s) first followed by chlorine(s).

made for the π^* energies, and good agreement was found between experimental and calculated π^* energies in all cases, except F₂C₂ClF, when the energies were evaluated by considering substitution of the fluorine(s) first followed by the chlorine(s). For F₂C₂ClF, the values resulting from two different orders of "construction" are presented in Table VI.

Table VI contains the energies of the π and π^* energies of nine chlorofluoroethylenes. Both experimental and calculated values are given, where the calculated values are described above. The last four molecules listed in Table VI, *cis*- and *trans*-1-chloro-2-fluoroethylene (*cis*- and *trans*-FHC₂ClH) and 1-chloro-*cis*-1,2-difluoroethylene (*cis*-FCIC₂FH) and 1-chloro-*trans*-1,2-difluoroethylene (*trans*-FCIC₂FH); have not been investigated in the vacuum ultraviolet; however, Momigny¹³ has reported their photoionization potentials, and from these data π energies have been evaluated and are compared with the calculated values. Chlorotrifluoroethylene (FCIC₂Cl₂) is also given in Table VI; however, no ionization potential is known for this compound. Therefore, no experimental π and π^* energies are available. The calculated value of the V ← N transition is the difference between the calculated π and π^* energies, and for FCIC₂Cl₂ this value is 54,596 cm^{-1} , which compares quite well with

(13) J. Momigny, *Nature (London)*, **199**, 1179 (1963).

the experimental value of the V ← N band maximum of 54,550 cm⁻¹.

Conclusions

In conclusion, several aspects of the results of the comparative method are summarized. (1) The initial large destabilization of the π orbital energy of ethylene on chlorine substitution is present in the chlorofluoroethylenes. (2) The initial large stabilization of the π^* orbital energy observed in the chloroethylenes is not present in the chlorofluoroethylenes. (3) There is a relatively strong π^* destabilizing effect present when halogen substitution occurs cis to a halogen present in the parent molecule (*i.e.*, the relatively large values of X_i for $i = 3, 5, 7,$ and 8). This suggests a geometry effect in the V state. This effect is observed in the

chlorofluoroethylenes as well as in the chloro- and fluoroethylenes. (4) The effects that halogen substitution exerts on the π and π^* orbital energies appear to be dependent on the kind of halogen substituted and on the positions, relative to the substituent, occupied by other halogens. The specific halogens present in the parent molecule do not appear to be a dominant factor.

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Ion-Molecule Reactions of 2-Butanol by Ion Cyclotron Resonance Spectroscopy

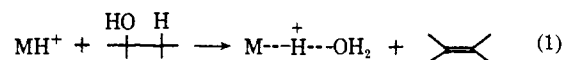
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Contribution No. 3966 from the Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91109, and the Department of Chemistry, University of California, Irvine, California 92664. Received March 17, 1971

Abstract: The reactions of 2-butanol with fragment ions generated from 2-butanol on electron impact have been studied by ion cyclotron resonance techniques. The reaction sequences involved are formulated from evidence obtained from double resonance experiments, the use of deuterium-labeled alcohols, and the measurement of single resonance ion intensities at 13 and 70 eV over a range of sample pressures (10⁻⁷-10⁻³ Torr). The gas-phase ion chemistry of 2-butanol, methanol, ethanol, 2-propanol, and *tert*-butyl alcohol is compared and reveals a remarkably systematic behavior characteristic of the hydroxyl functional group.

The gas-phase ion chemistry of several alcohols has been investigated by means of ion cyclotron resonance spectroscopy (icr) and high-pressure mass spectrometry.³⁻¹¹ The reactions of methanol,^{3,9-12} ethanol,^{10,11} 2-propanol,⁵ and *tert*-butyl alcohol^{4,6} have been reported in some detail, and some important similarities and differences in the ion chemistry of these alcohols have been noted. The present work describes the ion chemistry of 2-butanol which, from preliminary studies, indicated a sequence of reactions related to those observed for 2-propanol⁵ and *tert*-butyl alcohol.^{4,6}

Of particular interest is the dehydration of alcohols induced by ions possessing a labile proton (eq 1). This



reaction, while not observed for methanol or ethanol, is prominent in the ion chemistry of secondary and tertiary alcohols.⁴⁻⁶ A major objective of the present work was to investigate the dehydration reaction of eq 1 using deuterium-labeled 2-butanols in order to determine the relative yields of the various isomeric hydrocarbon products.

A second objective was to investigate the condensation reactions of 2-butanol. Reactions of this type are important in the ion chemistry of methanol and higher molecular weight alcohols and involve the elimination of one and sometimes two molecules of water from reaction intermediates. A pertinent example is the reaction of protonated acetaldehyde with 2-propanol as indicated in eq 2.^{5,8} The condensation reactions of labeled and unlabeled 2-butanols were examined in the present study in order to determine the possible structures of the reactant and product ions and to evaluate the nature of the processes by which the products are formed. Before discussing these reactions further, a

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