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Ionization and Dissociation of Perchlorylfluoride by Electron Impact

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Relative abundances and appearance potentials are reported for both positive and negative ions observed in the mass spectrum of perchlorylfluoride. Appearance potentials of the atom ions result in a value for $\Delta H_f(ClO_3F)$ of nearly zero within the experimental uncertainty. Bond dissociation energies and ionization potentials of the chloryl radicals are estimated from appearance potentials of the polyatomic ions. The energetics of probable ionization-dissociation processes are compared with observed data.

I. INTRODUCTION

UNTIL the recent preparation of perchlorylfluoride (ClO_3F),[1,2] the only compounds of chlorine, oxygen, and fluorine definitely known were the very reactive substances chloryl fluoride (ClO_2F) and fluorine perchlorate (ClO_4F). Further investigation showed that many of the properties of ClO_3F, particularly its chemical inertness and exceptional thermal stability, contrasted sharply with those of the other two substances.[3] This remarkable behavior suggested that a study of the ionization and dissociation of ClO_3F by electron impact methods would be worthwhile. It was hoped that the careful measurement of appearance potentials would lead to a reliable estimate of the heat of formation of the parent molecule. Since the present research was completed a report of the determination of the heat of formation of ClO_3F by thermochemical means has appeared.[4] Our results are in agreement.

II. EXPERIMENTAL

Mass spectra and appearance potentials were measured with a 180° mass spectrometer by means of previously described techniques.[5]

The ClO_3F vapor was handled by conventional apparatus since under normal conditions it appeared to be quite inert to hydrocarbon grease, sorbed water vapor, and the ordinary chamber and container materials.

Relative abundances of positive ions and of negative ions formed by ion-pair processes were measured with 70-v electrons. Abundances of negative ions formed by attachment processes were measured at electron energies of maximum cross section.

Argon was introduced simultaneously with the sample gas, and its spectroscopic ionization potential (15.7 ev)[6] was used to calibrate the ionizing voltage scale for the appearance potential measurements of the positive ions.

Appearance potentials were evaluated from semilog plots of positive ion current *versus* electron energy for the perchlorylfluoride ions and the A^+ ion of the calibrating gas. The limitations of this method for ions of low abundance or formed by complex processes have been discussed elsewhere.[7] Ionization efficiency curves for negative ions were plotted on a linear scale. The calibration of the ionizing voltage scale was by means of the O^- ion from CO. The small correction (about -0.2 ev) required to make the observed appearance potential conform with that reported by Hagstrum,[8] was assumed constant over the entire ionizing voltage range.

The highly purified sample of ClO_3F was very kindly provided through the cooperation of Dr. John F. Gall and G. Barth-Wehrenalp of the Pennsylvania Salt Manufacturing Company. Mass spectrometer analyses indicated no detectable impurities and it was estimated that they must be less than 0.1 percent.

III. RESULTS

The experimental data for both positive and negative ions are summarized in Table I. Column 1 lists the observed ions and column 2 gives the percent abundance relative to the most abundant ion as described in the previous section. All of the observed negative ions are formed by dissociative attachment processes. Several ions are formed by multiple processes some of which are of very low relative abundance. A resonance-type is observed for each process. Although the true width of these peaks is probably less than 0.1 ev,[9] a width of several volts was frequently observed in the present research probably resulting from an energy spread in the ionizing electron beam. The width of the peak makes difficult the positive identification of very low abundance ions and two possible attachment processes for the F^- ion are omitted from the table for this reason.

Column 4 lists the probable products of the ionization-dissociation processes consistent with the ob-

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[1] H. Bode and E. Klesper, Z. anorg. Chem. **266**, 275 (1951).

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[3] A. Engelbrecht and H. Atzwanger, J. Inorg. Nuclear Chem. **2**, 348 (1956).

[4] C. A. Neugebauer and J. L. Margrave, paper presented before the Fluorine Symposium of the Ind. Eng. Div., 130th meeting, American Chemical Society, Atlantic City, New Jersey, September 16–21, 1956. See Abstracts p. 28 M.

[5] V. H. Dibeler and R. M. Reese, J. Research Natl. Bur. Standards **54**, 127 (1955).

[6] C. E. Moore, Natl. Bur. Standards (U. S.) Circ. **467** (1949).

[7] Dibeler, Reese, and Mohler, J. Research Natl. Bur. Standards **57**, 113 (1956).

[8] H. D. Hagstrum, J. Chem. Phys. **23**, 1178 (1955).

[9] W. M. Hickam and R. E. Fox, Phys. Rev. **98**, 557 (A) (1955).

served energy involved. In most ambiguous cases, the process requiring the minimum energy is chosen because of the possibility of excess kinetic or excitational energy of the dissociation products. No search was made for ions formed with excess kinetic energy.

IV. DISCUSSION

The structure of the ClO_3F molecule was recently shown to be that of a C_{3v} symmetric top with the fluorine and 3 oxygens each bonded to the central chlorine atom.[10,11]

The observed mass spectrum is consistent with this structure even though only one polyatomic ion, ClO_2F^-, contains a fluorine atom, and no FCl ion was observed. An oxygen molecule ion is observed in both positive and negative spectra. This is probably the result of intramolecular rearrangement during the ionization-dissociation process. No metastable transitions were found.

The accurate measurement of the abundance of negative ions relative to positive ions is complicated by the reversal of the electric and magnetic fields and the necessarily critical focusing conditions. Nevertheless, the large relative abundance of negative ions formed by attachment of nearly zero-energy electrons is particularly noteworthy. This suggests that this compound may be valuable as a gaseous insulator as the attachment of slow electrons is considered to be one of the several important factors that contribute to the electrical-breakdown resistance of a gas.[12]

TABLE I. Relative abundances and appearance potentials of positive and negative ions in the mass spectrum of perchlorylfluoride.

Ion	Relative abundance (%)	Appearance potential (ev)	Probable products
ClO_3F^+	77.1	13.6 ± 0.2	ClO_3F^+
ClO_3^+	100.	14.3 ± 0.2	$ClO_3^+ + F$
ClO_2^+	36.6	15.7 ± 0.5	$ClO_2^+ + O + F$
ClO^+	16.1	18.0 ± 0.5	$ClO^+ + 2O + F$
O_2^+	1.9	$15.\pm1$	$O_2^+ + O + F + Cl$
Cl^+	18.6	23.0 ± 0.2	$Cl^+ + 3O + F$
O^+	10.5	22 ± 1	$O^+ + 2O + F + Cl$
F^+	0.9	27 ± 3	$F^+ + 3O + Cl$
ClO_2F^-	4.6	approx 0	$ClO_2F^- + O$
ClO_3^-	127.	approx 0	$ClO_3^- + F$
ClO_2^-	3.2	approx 0	$ClO_2^- + OF$
ClO_2^-	1.1	4.3 ± 0.3	$ClO_2^- + O + F$
ClO^-	0.06	2.4 ± 0.3	$ClO^- + O_2 + F$(?)
ClO^-	0.13	4.6 ± 0.3	$ClO^- + O + OF$(?)
ClO^-	0.06	8.5 ± 0.3	$ClO^- + 2O + F$(?)
O_2^-	0.1	3.2 ± 0.5	$O_2^- + Cl + OF$(?)
Cl^-	7.3	approx 0	$Cl^- + O_2 + OF$(?)
Cl^-	0.06	4.8 ± 0.3	$Cl^- + 2O + OF$(?)
O^-	0.8	3.7 ± 0.3	$O^- + ClO_2 + F$
O^-	0.2	7.4 ± 0.3	$O^- + ClO + O + F$(?)
F^-	86.	approx 0	$F^- + ClO_3$
F^-	8.6	4.3 ± 0.3	$F^- + ClO_2 + O$

No spectroscopic ionization potential of ClO_3F has been published. The electron impact value of 13.6±0.2 ev reported here represents the "vertical" ionization potential of the molecule as required by the Franck-Condon principle. It is an upper bound to the spectroscopic or "adiabatic" ionization potential.

The appearance potential of a positive fragment ion is equal to the sum of bond dissociation energies required to form the fragment plus the ionization potential of the fragment provided that the dissociation products are formed without excess kinetic, excitational, and vibrational energy. Direct computation of individual bond dissociation energies in perchlorylfluoride by means of this relation is not possible as ionization potentials are known only for the atoms and the oxygen molecule. However, several reasonable assumptions of dissociation processes permit the calculation of the heat of atomization and the heat of formation of the compound and lead to estimates of ionization potentials of the radicals.

Heat of Formation of ClO_3F

Previous studies of a variety of simple polyatomic molecules[5,7,13,14] indicate that positive atomic ions are frequently formed by the complete atomization of the molecule. This is assumed to be the process responsible for the formation of Cl^+ from ClO_3F. Hence, subtraction of the ionization potential of the chlorine atom (13.01 ev)[6] from the appearance potential of the Cl^+ ion (23.0±0.2 ev) yields 10.0±0.2 ev for the heat of atomization of ClO_3F. If next the atomic heats of formation of chlorine (1.26 ev),[15] of fluorine (0.82 ev),[15] and three times the heat of formation of the oxygen atom (2.56 ev)[16] are subtracted from 10.0±0.2 ev, the heat of formation (ΔH_f) of ClO_3F is found to be $-0.2_3\pm0.2$ ev. Similar though necessarily less reliable computations based on $A(O^+)=22\pm1$ ev, $A(F^+)=27\pm1$ ev, and $A(O_2^+)=15\pm1$ ev are consistent with this result. The value $\Delta H_f(ClO_3F)=-0.2_3\pm0.2$ ev or -5.3 ± 4 kcal/mole is in satisfactory agreement with the thermochemical value -5.0 kcal/mole reported recently by Neugebauer and Margrave.[4]

Ionization Potentials and Bond Dissociation Energies

The heat of formation of ClO_3 is reported to be +37 kcal/mole.[16] From this value, the value $\Delta H_f(ClO_3F)=-5$ kcal/mole, and the dissociation energy of F_2, the bond dissociation energy $D(O_3Cl-F)$ is found to be about 60 kcal/mole or 2.6 ev. This result is in agreement with 60 kcal/mole for the bond dissociation energy of

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[15] Evans, Munson, and Wagman, J. Research Natl. Bur. Standards **55**, 147 (1955).

[16] Rossini, Wagman, Evans, Levine, and Jaffe, Natl. Bur. Standards (U. S.) Circ. **500** (1952).

the ClF molecule.[15] Subtraction of $D(O_3Cl-F)=2.6$ ev from the appearance potential of the ClO_3^+ ion (14.3 ev) gives 11.7 ev for the ionization potential, $I(ClO_3)$, of the perchloryl radical. Although this value must be considered only as an upper limit because of the possibility of excess kinetic energy in the dissociation products, it is less than the ionization potential of the molecule and it is also quite close to the ionization potentials of the other chloryl radicals, ClO_2 and ClO, as discussed below.

The heats of formation reported for ClO_2 and ClO are $+25.0$ kcal/mole and $+33.0$ kcal/mole,[16] respectively. If it is assumed that the other dissociation products formed along with ClO_2 and ClO are atomic, as shown in column 4 of Table I, the calculated dissociation energies are $D(O_2Cl-O,F)=107$ kcal/mole or 4.6 ev and $D(OCl-2O,F)=174$ kcal/mole or 7.6 ev, respectively. If these values are subtracted, respectively, from $A(ClO_2^+)=15.7$ ev and $A(ClO^+)=18.0$ ev, upper limits to the ionization potentials $I(ClO_2)=11.1$ ev and $I(ClO)=10.4$ ev are obtained. The formation of molecular instead of atomic dissociation products would result in markedly higher ionization potentials for both radicals.

The calculated dissociation energies $D(O_3Cl-F)=60$ kcal/mole, $D(O_2Cl-O,F)=107$ kcal/mole, and $D(OCl-2O,F)=174$ kcal/mole enable an estimate of the average Cl—O bond dissociation energy to be made. It is about 57 kcal/mole, and therefore quite close not only to the Cl—F bond dissociation energy discussed earlier but also to the bond dissociation energy (63.0 kcal/mole) of the ClO molecule.[17]

Negative Atomic Ions

The appearance potential of a negative ion, $A(R^-)$, formed by dissociative attachment is equal to the energy required for the dissociation process minus the electron affinity of the fragment, $EA(R)$, plus excess energy. Again assuming the absence of excess energy terms, bond dissociation energies can be estimated when electron affinities are known. Unfortunately, in the present case, the appearance potentials of negative atom ions cannot be used to compute independently the energy of atomization, as negative atom ions in perchlorylfluoride are apparently formed by processes that energetically could not involve complete atomization of the molecule. For example the Cl^- ion is formed by two dissociative attachment processes appearing at electron energies of "zero" and 4.8 ev. On the basis of previously defined constants, and $D(F-O)=2.5$ ev* obtained from $\Delta H_f(F_2O)$,[14] the process of minimum dissociation energy (about 2.5 ev) is that indicated in column 4 of the Table. As $EA(Cl)=3.75$ ev,[18] the process is probably that shown and the ionization-dissociation products are formed with about 1.3 ev excess energy. The voltage interval between the first and second appearance potentials (4.8 ev) is nearly equal to the dissociation energy of the oxygen molecule and suggests the products listed in column 4.

Two attachment processes are observed for the O^- ion. The calculated appearance potential for the first process is equal to the average $D(Cl-O)=2.7$ ev obtained from the dissociation energy of ClO,[17] plus $D(Cl-F)$ previously computed, less the $EA(O)=1.48$ ev[19] or approximately 3.8 ev compared with the observed 3.7 ev. Although the voltage interval between the first and second appearance potentials (3.7 ev) is greater than the estimated energy required to dissociate a second Cl—O bond, the dissociation products may be formed with excess energy.

Two attachment processes are definitely identified for the F^- ion. For the first process appearing at "zero" electron energy, the $EA(F)=3.62$ ev[18] represents an upper limit to the $D(O_3Cl-F)$. The previously computed value of 2.6 ev for this bond dissociation energy suggests the products may be formed with approximately 1.0 ev excess energy. The second appearance potential is greater than that expected from the average Cl—O bond energy and may again represent excess energy of the dissociation products. At least one other attachment process for F^- was tentatively considered as corresponding to further dissociation of Cl—O bonds but omitted from the Table because of uncertain identification.

Negative Polyatomic Ions

A single attachment process is observed for the ClO_2F^- ion appearing at nearly "zero" electron energy. Although the electron affinity of this radical is unknown, a low limit is given by the previously estimated Cl—O bond dissociation energy; i.e., $EA(ClO_2F)\geq 2.7$ ev.

Pritchard[18] has tabulated the electron affinities of ClO_3 (4.0 ev), ClO_2 (3.4 ev), and ClO (2.9 ev). As the ClO_3^- ion is formed by a single attachment process with $A(ClO_3^-)\approx 0$, the electron affinity of ClO_3 also represents an upper limit to the O_3Cl-F bond dissociation energy of 2.6 ev calculated above.

Of the two appearance potentials observed for the ClO_2^- ion, the process appearing at nearly "zero" electron energy is unambiguous and, as in the case of the minimum energy process for the Cl^- ion, requires the postulate of the OF fragment. The minimum energy required for the process results from $D(Cl-O)$ plus $D(Cl-F)$ less $D(O-F)$, or 2.8 ev. As $EA(ClO_2)=3.4$ ev is an upper limit to the process, the products may be formed with 0.6 ev excess energy. The voltage

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[17] A. G. Gaydon, *Dissociation Energies and Spectra of Diatomic Molecules* (Chapman and Hall, Ltd., London, 1953), second edition.

* There is no previous evidence for the existence of the diatomic molecule, FO. However, the postulate is energetically satisfactory in this and several subsequent processes.

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[19] S. J. Smith and L. M. Branscomb, J. Research Natl. Bur. Standards **55**, 165 (1955).

interval between the first and second appearance potentials is greater than expected from $D(O-F)$ or $D(Cl-O)$ and may again indicate excess energy.

The voltage intervals between the three appearance potentials observed for the ClO^- ion correspond approximately with the difference in energy required by the indicated dissociation processes. For absolute agreement between computed and observed values, however, several volts excess energy must be assumed in each case.

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Infrared Spectrum of Hydrogen Sulfide in the 2.6-Micron Region*†

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The infrared absorption spectrum of hydrogen sulfide (H_2S), in the region from 3730 cm^{-1} to 4030 cm^{-1}, has been measured under high resolution. Calibration was made from emission lines of argon, observed in the second order, using Edser-Butler bands. The absorption has been assigned to two overlapping combination bands, a type A band $(n_1,n_2,n_3)=(0,1,1)$ at 3789.07 cm^{-1}, and a type B band (1,1,0) at 3779.23 cm^{-1}, plus overlapping water vapor absorption. The excited state inertial parameters in cm^{-1} giving the best fit to the data were found to be

	A^*	B^*	C^*
(0,1,1)	10.517	9.124	4.619
(1,1,0)	10.595	8.985	4.603

INTRODUCTION

A PARTIAL resolution of the absorption bands of hydrogen sulfide in the 2.6 μ region was described by Nielsen and Barker[1] in 1931. A later investigation was made with improved resolution and reported by King and Hainer[2] in 1948. In the latter case an analysis was made by punched-card methods and the absorption was assigned to a type A band.

This region has been re-investigated under high resolution (≈ 0.15 cm^{-1}) and the fine structure analyzed. To account for the observed absorption, it was found necessary to assign it to two overlapping bands, one of type A with the change of electric moment parallel to the axis of least moment of inertia, and the other of type B with the change of electric moment parallel to the axis of intermediate moment of inertia (the figure axis for H_2S).

EXPERIMENTAL

A vacuum grating spectrometer was used to obtain the spectra. It utilizes a zirconium arc source, a 15 000 lines per inch echelette grating in a monochromator with Pfund[3] type optics, and a lead sulfide detector. The observed resolution limit was ≈ 0.15 cm^{-1} in this region.

A multiple traverse cell of the J. U. White[4] type was used to give an absorption path length of about 3 meters. Spectra were run at various pressures up to 14 cm Hg in order best to observe various regions of the band.

The hydrogen sulfide was obtained from the Matheson Company and part of the water vapor contained in the sample was removed by passing it through a trap cooled by a mixture of dry ice and acetone.

For calibration of the spectra a Fabry-Perot etalon was placed in a parallel beam in the vacuum spectrometer just before the entrance to the monochromator. This arrangement produces, in conjunction with the monochromator, infrared Edser-Butler bands with equal wave-number spacing. These bands were used as markers to interpolate between two emission lines of argon of frequencies 7478.84 cm^{-1} and 8060.43 cm^{-1},[5] the second order of which appear prominently superposed on all our records.

ANALYSIS

A portion of the spectrum of hydrogen sulfide is reproduced in Fig. 1. At much lower pressures the gathering of lines in the vicinity of 3790 cm^{-1} is a prominent feature of the band. Dennison[6] has shown that type A bands lead to a gathered Q branch, and type B bands do not lead to such a gathered Q branch. (Type C bands do not exist for H_2S or any other triatomic

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‡ Now at the Scientific Laboratory, Ford Motor Company, Dearborn, Michigan.

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