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The Mass Spectra of Chromyl Chloride, Chromyl Chlorofluoride and Chromyl Fluoride

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The results of a mass spectrometric study of CrO_2Cl_2, CrO_2ClF and CrO_2F_2 are reported. The fragmentation patterns of each compound in the normal and dimeric mass range and the appearance potentials of the positive ion fragments of CrO_2Cl_2 and CrO_2F_2 are given. A method of taking appearance potential data is presented which results in the appearance potential curves of all fragments having nearly identical slopes and also permits taking data when the ion currents are changing slowly.

Introduction

Chromium is one of the elements on which no work has been done to determine whether or not the isotope abundance is dependent on geological deposition. The element is widely distributed throughout the world principally as the ore, chromite, which generally is found in pre-Cambrian deposits. The volatility of the easily prepared and well known compound CrO_2Cl_2 simplifies the sample handling problem associated with the mass spectrometry. A mass spectrometer capable of handling corrosive gases of high mass was available in our laboratory and so chromite ore samples were collected from well characterized deposits throughout the world.[1] No knowledge of the behavior of chromyl halides in the mass spectrometer was available, so a study of the fragmentation pattern of CrO_2Cl_2 was undertaken to determine the best ion fragments for isotope abundance work and the extent of possible interferences. The parent ion appeared the most logical to use for isotope abundance measurements. However, large discrepancies in the isotope abundances from those expected to have been present (using known Cl and O abundances and measured Cr^+ abundances) were observed when the parent ions were employed in the measurement. This caused doubt concerning the validity of such measurements. Since these discrepancies could only have been caused by ion fragments of a possible dimeric species, the heavy mass region was investigated and dimeric chromium oxychloride was discovered. This also gave rise to a fragmentation pattern and the interference observed in the parent monomer ions. In looking for a more suitable compound, chromyl fluoride (CrO_2F_2) was prepared and its normal and dimeric fragmentation patterns were studied. This led to the chance discovery of chromyl chlorofluoride, CrO_2ClF, which was found in the mass spectrometer, and presumably was due to reaction between CrO_2F_2 and adsorbed CrO_2Cl_2. Attempts to explain the difference in fragmentation patterns between the similar chromyl compounds made a study of the appearance potentials of the various fragments advisable. The results of these studies are presented in this paper. Results of the isotope abundance work will be presented in a future publication.

Experimental

All measurements were made on a 180 degree mass spectrometer with a five inch radius (Consolidated Electrodynamics Corporation mass spectrometer, model CEC 21-220). It was modified to permit magnetic as well as electrostatic scanning. Magnetic scanning was used exclusively in these measurements. The ionizing current was 150 μa., and the scans were made using 1600 volt ions. Electron accelerating voltages were measured with a Rubicon Potentiometer, Type 2700, placed across a 1:100 voltage divider. Argon was used as the calibrating gas in the appearance potential measurements.

Because of the corrosive nature of the gases, a constant gas flow into the analyzer was difficult to achieve. This resulted in data for the appearance potential work which was not constant and subject to considerable spread. The difficulty was overcome by measuring the ion currents at some reference electron accelerating voltage immediately before a measurement at the desired electron voltage, thus enabling corrections to be made for any possible change in gas flow during any particular data-collecting experiment. The electron accelerating voltage for this instrument was supplied from a ten-turn helical potentiometer placed across a 150 volt voltage-regulator tube. To facilitate the change from one electron voltage to another, a second helical potentiometer and a switching device (Fig. 1) were added to the filament circuit. One potentiometer was adjusted to some reference voltage. The second potentiometer was then varied to supply any desired voltage. The switching device allowed the operator to choose either potentiometer as the source of voltage for electron acceleration. In taking data, the variable voltage was adjusted to the desired value, the filament was switched to the reference voltage and the ion current recorded. Then the filament was switched to the variable voltage and the resulting second ion current recorded. The ratio of the ion current at the variable voltage to that at the reference voltage was plotted against the changing voltage to give the ionization efficiency curve.

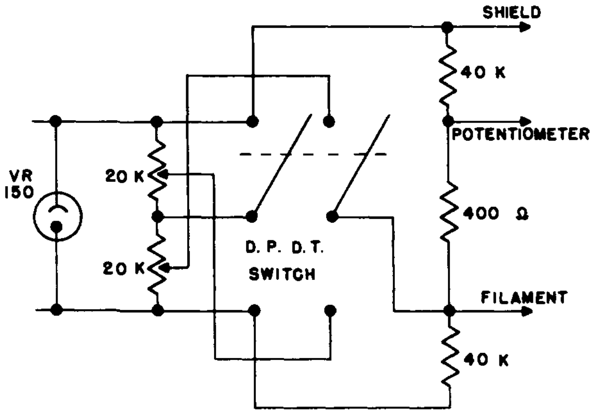

Fig. 1.—Filament voltage switching device.

The actual method employed in taking data was according to the following procedure. The reference voltage was set at 50 volts and the ion current ratios were recorded at five-volt intervals from this value. A plot of these data yielded a rough curve. A new reference point was chosen at the upper end of the straight line portion of the curve at the point where the curve started to deviate from the straight line. With this new reference point, more precise data were taken at smaller accelerating voltage intervals. The curves in Fig. 2 were obtained by this method.

This method of presenting data makes it possible to compare the general characteristics of ionization efficiency

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[1] The coöperation of Dr. W. H. Hartford of the Mutual Chemical Company in gathering the samples is acknowledged.

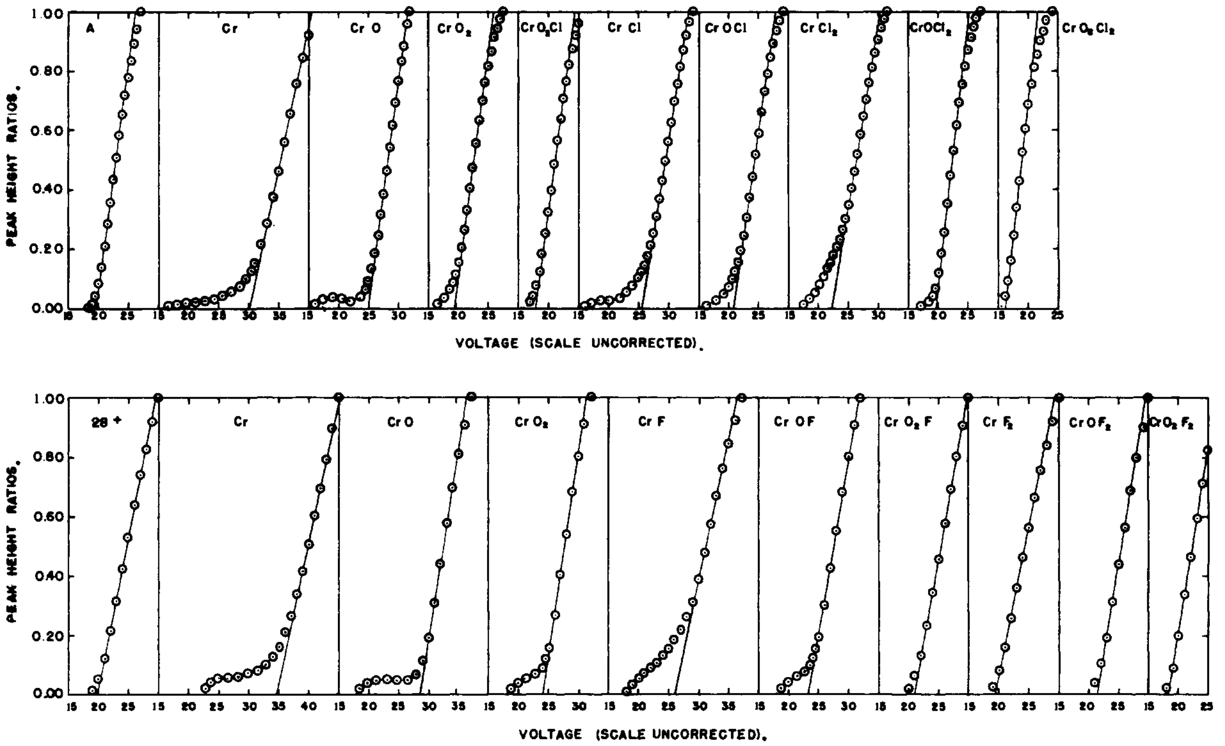

Fig. 2.—Ionization efficiency curves for positive ion fragments of chromyl chloride and chromyl fluoride.

curves on the same scale without resorting to any mathematical manipulation other than that involved in taking the ratios. It is also possible to make comparisons with similar curves obtained for standard substances, such as argon, since the plots are generally parallel. Extrapolation of the straight line portions of the curves[2] in Fig. 2 gives values for the intercept relative to a value of 15.7 e.v. for argon. These values are listed in Table I.

TABLE I

INTERCEPT POTENTIALS OF THE CHROMYL HALIDE POSITIVE ION FRAGMENTS

Fluoride		Chloride	
Ion	Intercept potential,[a] e.v.	Ion	Intercept potential,[a] e.v.
CrO_2F_2	14.0 ± 0.2	CrO_2Cl_2	12.6 ± 0.3
CrO_2F	16.3 ± .3	CrO_2Cl	13.9 ± .3
CrO_2	19.8 ± .2	CrO_2	15.2 ± .5
$CrOF_2$	16.8 ± .4	$CrOCl_2$	15.8 ± .2
CrOF	19.8 ± .2	CrOCl	17.0 ± .3
CrO	24.4 ± .2	CrO	21.4 ± .2
CrF_2	14.8 ± .2	$CrCl_2$	18.2 ± .2
CrF	21.7 ± .4	CrCl	22.2 ± .2
Cr	30.8 ± .2	Cr	26.7 ± .2

[a] Limits set down in this table represent the precision obtained for several measurements on each of the ion fragments. All data have been corrected to an intercept value of 15.7 e.v. for argon.

Fragmentation Patterns.—The fragmentation patterns of the three chromyl compounds were determined at an electron accelerating voltage of 70 volts and an ion accelerating voltage of 1600 volts. The results are shown in Table II.

The fluoride and chloride patterns were obtained from the pure compounds. The pattern for the mixed halide was obtained from an equilibrium mixture[3] according to the equation

$$CrO_2Cl_2 + CrO_2F_2 = 2CrO_2ClF$$

Because of this equilibrium, the chlorofluoride cannot be prepared in pure form and so its fragmentation pattern had to be determined from the equilibrium mixture of the three compounds. To accomplish this, the complete spectrum of the mixture was first determined. Purity of the spectrum was established by taking the currently accepted isotope abundances of Cr, O, Cl and F and calculating the expected ion current peak heights of all possible fragments of each isotopic species. These were then compared with the observed peak heights. Where several fragments had the same mass, the contribution of each fragment was determined by the use of simultaneous linear equations. The peak heights so calculated for each mass agreed with those observed within 2% of the observed peak height. The amounts of each fragment ion present were taken to be those calculated. From the fragmentation pattern of the fluoride and chloride, the contribution of each of their fragment ions was known. These were subtracted from the measured amounts of each ion fragment of the mixture. The residue was assumed to be the amount of fragment ions formed from the chlorofluoride. The values listed for the chlorofluoirde in Table II were obtained from a mixture whose ion currents were in the ratio

$$CrO_2F_2 : CrO_2ClF : CrO_2Cl_2 :: 7 : 18 : 13.$$

TABLE II

FRAGMENTATION PATTERNS FOR THE CHROMYL HALIDES

Fluoride		Chlorofluoride		Chloride	
Ion	Abundance	Ion	Abundance	Ion	Abundance
CrO_2F_2	47	CrO_2ClF	100	CrO_2Cl_2	100
CrO_2F	23	CrO_2Cl	61	CrO_2Cl	51
CrO_2	1	CrO_2F	1	CrO_2	12
		CrO_2	1		
$CrOF_2$	40	CrOClF	13	$CrOCl_2$	4
CrOF	21	CrOCl	35	CrOCl	25
CrO	6	CrOF	6	CrO	14
		CrO	9		
CrF_2	100	CrClF	13	$CrCl_2$	4
CrF	18	CrCl	20	CrCl	12
Cr	29	CrF	4	Cr	33
		Cr	30		

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(2) R. H. Vought, *Phys. Rev.*, **71**, 93 (1947).

(3) G. D. Flesch and H. J. Svec, THIS JOURNAL, **80**, 3189 (1958).

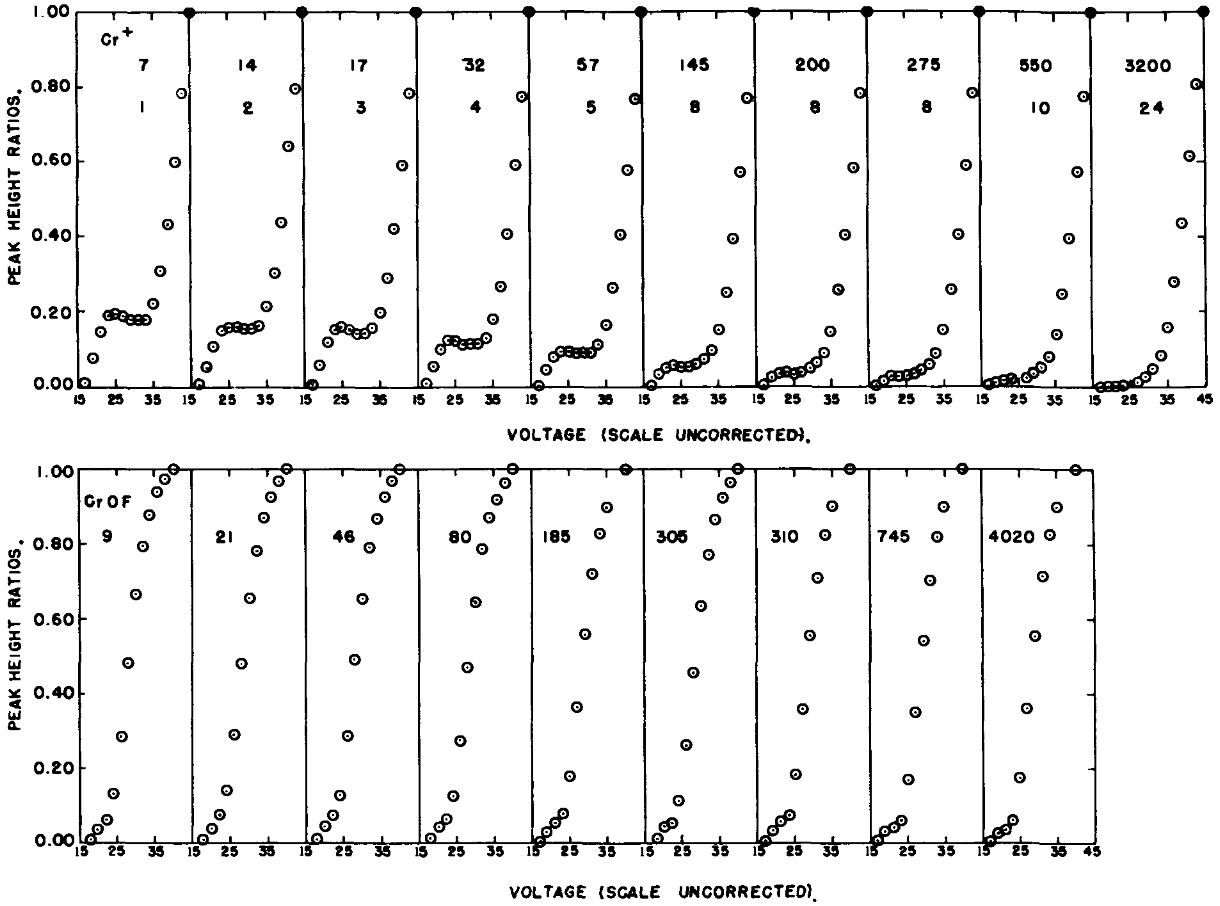

Fig. 3.—Ionization efficiency curves of Cr^+ and $CrOF^+$ of chromyl fluoride at various pressures.

They were checked by calculating and measuring the ion currents of a mixture whose ratio was 16:8:1. The average error between the calculated and observed ion currents was less than 3%.

Two peculiarities are noteworthy in the cracking patterns. The CrF_2^+ ion is twice as abundant as the parent, $CrO_2F_2^+$, and the abundances of the chloride fragments of the chlorofluoride are larger than those of the corresponding fluoride fragments.

Dimeric Species.—The dimer mass region of the pure chloride, the pure fluoride and a mixture of the two had the ions and abundances listed in Table III. These were identified from the mass and isotopic variations of the ions. The total dimer current was about 0.1, 0.1 and 0.3% of the total positive ion current of pure chloride, pure fluoride and mixture, respectively. Experiments to determine the nature or origin of the compounds causing these ions were inconclusive. The data strongly suggest that dimeric compounds exist as distinct molecular species mixed with the monomers.

TABLE III

FRAGMENTATION PATTERNS OF CHROMYL HALIDE POSITIVE IONS IN THE DIMER REGION

Fluoride		Chlorofluoride		Chloride	
Ion	Abundance	Ion	Abundance	Ion	Abundance
$Cr_2O_2F_4$	100	$Cr_2O_5F_2$	12	$Cr_2O_4Cl_3$	100
		Cr_2O_5F	10	$Cr_2O_4Cl_2$	45
		$Cr_2O_4F_3$	75	Cr_2O_4Cl	52
		$Cr_2O_4F_2Cl$	100	$Cr_2O_3Cl_3$	3
		$Cr_2O_4FCl_2$	70	Cr_2O_3Cl	12
		$Cr_2O_4Cl_3$	16	$CrOCl_3$	30
		$Cr_2O_4F_2$	14		
		$Cr_2O_4Cl_2$	14		
		$Cr_2O_3F_3$	6		
		$Cr_2O_2F_4$	16		

Ionization Efficiency Measurements.—The ionization efficiency curves for many of the ion fragments shown in Fig. 2 are similar to those for CH_2^+ observed in the spectrum of methane.[4] Thus one is led to suspect that several processes may be responsible for the formation of these ions. The voltage separation of the two breaks should be a measure of the difference in potential of the two processes responsible for the ions. In some cases, especially the Cr^+ curves, it is difficult to assign any reasonable processes to the different breaks because of the large voltage differences (15–18 e.v. for Cr^+). However, a study of the pressure dependence for the curves of Cr^+, CrO^+ and $CrCl^+$ of the chloride and Cr^+, CrO^+, CrF^+ and $CrOF^+$ of the fluoride showed that two distinct breaks were significant only for $CrOF^+$. In the others, the ion currents at the lower electron voltages were relatively constant over a wide range of pressure. This indicates that the source of these ions is not due to direct electron bombardment of the sample gas or any contained gaseous impurity. Since there was no background at the masses involved, the ions probably resulted from an apparent zero-order reac-

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[4] C. A. McDowell and J. W. Warren, *Disc. Faraday Soc.*, "Hydrocarbons," **10**, 53 (1951).

tion of the sample gas with something in the sample inlet system, ion source or analyzer system of the spectrometer. If adsorption of some species is the primary process on which these ions depend and the adsorbing surface is only partially covered at low pressures, a first-order pressure dependence is expected. At higher sample pressures the surface should be completely covered, with the resulting effect being the apparent zero-order dependence observed. Support of this thesis was given by an experiment in which the sample gas pressure in the source was greatly reduced. At pressures from $^1/_{500}$ to $^1/_{200}$ of the normal operating pressure, the ion currents at lower electron accelerating voltages varied directly as the pressure.

It is interesting to note that the initial break of the ionization efficiency curves for all the ion fragments exhibiting an apparent double break was 12.5 ± 0.5 volt for fluoride fragments and 11.5 ± 0.5 volt for the chloride fragments. This small variation suggests that these fragment ions may be of thermal origin and not primarily due to electron bombardment of gaseous molecules.

Figure 3 shows the Cr^+ and $CrOF^+$ curves as they appeared at various pressures. The upper number of each Cr^+ curve is the relative ion current for 45-volt electrons. The lower number is the value at 25 electron volts. The number on the $CrOF^+$ curve is the relative ion current for 45-volt electrons.

It would be tempting to interpret these results in terms of the bond strengths in molecular or ionic chromyl halides. However, the paucity of ionization potential data for CrO^+ or CrX^+, coupled with the uncertainties involved in interpreting such data as presented in Figs. 2 and 3, make any such attempts tenuous. It is apparent that no simple assumptions can be made which represent the processes occurring in the mass spectrometer ion source. While the results listed in Table I appear to have some consistency, their meaning in terms of thermodynamic properties in these molecules is clouded by the several likely processes which may be occurring.

Attempts to measure ionization efficiencies of the chlorofluoride fragment ions were unsuccessful, except for the parent ion. The value of 14.0 ± 0.2 volt was obtained for the appearance potential from a measurement on a mixture containing very little chloride. The amount of chlorofluoride present was large enough to give reliable results, and the very small amount of $CrOCl_2^+$ from the chloride did not interfere.

It was thought that the appearance potential curves for some of the ions of a mixture of all three compounds might exhibit two or more "breaks" because of the probable difference in appearance potential of the ions which are common fragments of two or all of the compounds. In the course of work reported here, no such breaks were observed on any mixture.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

Iron(III) Complexes in Non-aqueous Solvents. I. The Solvolysis and Chloride Complex Constants in N-Methylacetamide

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Spectrophotometric measurements yielded values of 1.4×10^{-3} mole liter^{-1} for the first solvolysis constant of Fe^{+3} and 7.5×10^2 and 13 liter mole^{-1} for the stepwise formation constants of $FeCl^{+2}$ and $FeCl_2^+$, respectively, in N-methylacetamide. The molar extinction coefficients at 563 mμ of FeS^{+2} (where S^- is the solvent anion), $FeCl^{+2}$ and $FeCl_2^+$ were found to be 1.8×10^3, 1.9×10^3 and 9.3×10^3, respectively. The average latent heat of vaporization of N-methylacetamide over the temperature interval from 115 to 205° was 14.2 kcal. mole^{-1}.

Experiments, preliminary to an investigation of the kinetics of the Fe(II) + Fe(III) isotope exchange reaction in the solvent N-methylacetamide (NMA), showed that Fe^{+3} formed complexes with the anions of various strong mineral acids in this solvent. In Fig. 1 are shown spectra of anhydrous $FeCl_3$ dissolved in NMA in the presence of 0.1 *M* hydrochloric, perchloric and sulfuric acids and in the absence of any added acid. Presence of water up to at least one molar had no appreciable effect on these spectra. Apparently complexes between Fe^{+3} and the various anions are formed which have different absorption spectra. Therefore, before the rate constants for the isotopic exchange of iron between Fe(II) and the various Fe(III) complexes could be determined, it was necessary to determine the association constants of some of these complexes and to determine the solvolysis constant of Fe^{+3} in NMA.

The solvent NMA was chosen because it could be obtained in relatively anhydrous condition (water concentration less than 0.002 *M*) and because of its high dielectric constant.

Experimental

Reagents.—Iron(III) chloride was prepared by passing dry Cl_2 gas at room temperature through iron powder in the presence of a trace of moisture. The product was analyzed iodometrically and found to contain 96.8% $FeCl_3$. The main impurity probably was water; the amount of water introduced with the $FeCl_3$ in making a 0.1 millimolar solution of Fe(III) was thus much less than the minimum water content which could be detected by a Karl Fischer titration.

Hydrochloric acid solutions were prepared by passing dry HCl gas[1] into NMA. The solutions were standardized by diluting an aliquot at least twofold with water and titrating with standard NaOH using phenolphthalein as indicator.

Standard NaCl solutions were prepared by dissolving an-

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(1) "Inorganic Syntheses," Vol. 1, McGraw-Hill Book Co., Inc., New York, N. Y., p. 117.