Mass Spectrometry of Perchloric Acid and the Oxides of Chlorine

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The mass spectra of Cl_2, HCl, $HClO_4$, Cl_2O_7, ClO_2, Cl_2O_6, and Cl_2O have been determined at 70 electron volts using a Bendix time-of-flight mass spectrometer. Extreme care was taken to exclude impurities. The results are compared with other reported spectra.

TO INTERPRET the mass spectra of the products of several perchlorate decompositions, the standard reference spectra of perchloric acid, the chlorine oxides, and related compounds were needed. These spectra were measured on a Bendix Model 12 mass spectrometer with 70-volt electrons. The spectra were recorded on a strip chart recorder, and are listed in Table I.

EXPERIMENTAL

All preparations and transfers were made in the presence of borosilicate glass, Teflon, and stainless steel. Momentary passage through a brass needle valve into the mass spectrometer was necessary for some runs. The system was scrupulously free of organic matter and no explosions were observed.

With the exception of the second method for the preparation of Cl_2O, all preparations were adapted from those listed by Brauer (*1*). Suitable modifications were made for the micro quantities involved and to ensure a minimum of water and air in the sample.

The materials, as reported in the literature, were in the main unstable, as shown by the fact that excessive transfers led to the appearance of impurities in the spectra. Large samples also tended to show impurity peaks. Other than the colors, which were in agreement with those reported (*1*), no further physical properties were determined, as the mass spectra were considered to be a far more sensitive test for purity than melting points or vapor pressures.

Cl_2. The material was taken from a commercial tank, condensed on BaO at −196° C., and pumped. The spectrum was measured on material volatile at −80° C. and introduced to the mass spectrometer through a needle valve. No HCl was observed in the spectrum.

HCl. The HCl was taken from a commercial tank and condensed at −196° C. The spectrum was measured on material volatile at −110° C. and introduced to the mass spectrometer through a needle valve.

$HClO_4$. The $HClO_4$ was prepared from H_2SO_4 (95%) and $Mg(ClO_4)_2$. The spectrum was taken directly from the mixture at −21° C. No Cl_2O_7 was seen in the spectrum.

Cl_2O_7. The Cl_2O_7 was prepared from oleum and $Mg(ClO_4)_2$ at room temperature. The volatile product was distilled under vacuum several times until the sulfur-containing species were no longer seen in the spectrum. The vapors were dried with P_2O_5. The spectrum was taken from −30° C. through a needle valve. The intensity of the $HClO_4^+$ ion was less than 0.1% of the base peak of Cl_2O_7.

ClO_2. The ClO_2 was prepared from $KClO_3$ and H_2SO_4 at 0° C. The product was condensed at −196° C. The temperature was raised to −80° C. and the material pumped for a short time. The spectrum was taken from the material volatile at −80° C. and introduced to the mass spectrometer through a needle valve. No chlorine was observed in the spectrum.

Cl_2O_6. The Cl_2O_6 was prepared from ClO_2 and O_3. The O_3 was prepared in a commercial ozonizer and carried in an O_2 stream. All gases were dried with $Mg(ClO_4)_2$. The carrier gases (O_2 and He) were dried at −80° C. on glass beads. The Cl_2O_6 was formed at 0° C. on glass beads and condensed at −21° C. The material was pumped at −21° C. for an extended time to a high vacuum. The material volatile at 0° C. was introduced to the mass spectrometer through a needle valve. A trace of $HClO_4$ was observed in the spectrum and the necessary correction was made. However, no Cl_2O_7 was seen.

Cl_2O. The Cl_2O was prepared in two ways:

METHOD 1. The reaction was carried out between dried powdered HgO supported on glass beads at 0° C. and Cl_2 dried with P_2O_5. The products were condensed at −80° C. and fractionated under reduced pressure in a reflux column operating between −50° and −80° C. The refluxing was continued with occasional sampling and removal of condensate until a constant spectrum was obtained. The Cl_2O was introduced directly into the mass spectrometer from the column through a nearly closed Fischer-Porter valve.

METHOD 2. The Cl_2O was also prepared by the method of Schack and Lindahl (*7*). The spectrum was run on the gas evolving directly from an excess of HgO. The spectra measured from material volatile at −110° and −78° C. were the same within experimental scatter as the spectra of the Cl_2O prepared by Method 1.

RESULTS AND DISCUSSION

The results are shown in Table I. The spectra for HCl and Cl_2 are shown for comparison. The pattern coefficients were reproducible to ±5%.

In contrast to other spectra on oxychlorine compounds (*3, 4, 6*), no CO_2 was seen in these spectra. This is undoubtedly due to the care taken to exclude all organic materials except Teflon, as well as to an uncarbonized filament in the mass spectrometer. The mass spectrometer background, other than water, air, and an Ar standard, was practically nonexistent. The ion source is an

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Table I. Mass Spectra of Chlorine Compounds

Mass	Ion Species	$HClO_4$	Cl_2O_7	Cl_2O_6	ClO_2	Cl_2O	Cl_2	HCl
16	O^+	0.023	0.0080	0.038	0.052	0.0088	[a]	...
17	OH^+	0.026	[b]	...	...	...	...	...
17.5	$^{35}Cl^{++}$	...	...	...	0.0004	0.0050	0.0074	[c]
18.5	$^{37}Cl^{++}$	...	...	...	0.0001	0.0017	0.0024	[c]
32	O_2^+	0.033	0.020	0.083	0.042	...	...	...
35	$^{35}Cl^+$	0.085	0.013	0.041	0.063	0.250	0.183	0.174
36	$H^{35}Cl^+$	0.020	[b]	...	...	...	0.0157	1.000
37	$^{37}Cl^+$	0.027	0.0040	0.013	0.021	0.078	0.051	0.054
38	$H^{37}Cl^+$	0.0063	[b]	...	...	...	...	0.311
51	$O^{35}Cl^+$	0.199	0.110	0.324	0.449	1.000	...	...
52	$HO^{35}Cl^+$	0.018	[b]	[d]	[d]	[d]	...	...
53	$O^{37}Cl^+$	0.064	0.035	0.098	0.142	0.312	...	...
54	$HO^{37}Cl^+$	0.0064	[b]	[d]	[d]	[d]	...	...
67	$^{35}ClO_2^+$	0.574	0.312	1.000	1.000	...	...	...
68	$H^{35}ClO_2^+$	0.021	[b]	[d]	[d]	[d]	...	...
69	$^{37}ClO_2^+$	0.182	0.099	0.322	0.319	...	...	...
70	$H^{37}ClO_2^+$, $^{35}Cl_2^+$	0.0079	[b]	[d]	[d]	0.090	1.000	...
72	$^{35}Cl^{37}Cl^+$	...	...	...	...	0.057	0.627	...
74	$^{37}Cl_2^+$	...	...	...	...	0.0097	0.089	...
83	$^{35}ClO_3^+$	1.000	1.000	0.089	...	...	...	...
84	$H^{35}ClO_3^+$	0.011	...	...	...	...	...	...
85	$^{37}ClO_3^+$	0.327	0.319	0.032	...	...	...	...
86	$H^{37}ClO_3^+$, $^{35}Cl_2O^+$	0.0036	...	...	...	0.391	...	...
88	$^{35}Cl^{37}ClO$	...	...	...	...	0.257	...	...
90	$^{37}Cl_2O^+$	...	...	...	...	0.045	...	...
99	$^{35}ClO_4^+$	None[e]	0.00044	...	...	...	...	...
100	$H^{35}ClO_4^+$	0.661	...	...	...	...	...	...
101	$^{37}ClO_4^+$	None[e]	0.00013	...	...	...	...	...
102	$H^{37}ClO_4^+$	0.214	...	...	...	...	...	...
182	$^{35}Cl_2O_7^+$	...	0.00088	...	...	...	...	...
184	$^{35}Cl^{37}ClO_7^+$	...	0.00051	...	...	...	...	...
186	$^{37}Cl_2O_7^+$	...	0.00009	...	...	...	...	...

[a] ..... <0.001 above background.
[b] <0.001 above background after removal of $HClO_4$ pattern.
[c] Not measured.
[d] <0.01 above background.
[e] <0.0001 above background.

open structure, and effective at room temperature. This is in contrast to other mass spectrometers which have enclosed ion sources which are often heated. A pressure of 5×10^{-7} torr of a constant Ar leak was used to calibrate the multipliers. During an analysis, the pressure was never above 5×10^{-6} torr. This combination of low pressure, open ion source, and room temperature reduces the chance of decomposition prior to ionization. This is shown by the differences between this spectrum for $HClO_4$ and the spectra of Heath and Majer (*6*) and of Fisher (*2*) for both $HClO_4$ and ClO_2. They observed more HCl^+ and more O_2^+ fragments than did the present authors. Some decomposition was noted in that with the Philips gage on, the 32 and 16 peaks showed sudden bursts. These peaks were steady with the gage off. The rest of the spectrum was unaffected by the Philips gage. This effect was noted for all of the oxychlorine compounds.

The protonated species HOCl and $HClO_2$ were noted among all of the oxides, even when $HClO_4$ was absent. For Cl_2O, Cl_2O_7, and ClO_2, the protonated peak heights were small ($\sim 10^{-2}$ of the major peak) and were ignored. For ClO_3, the peaks were somewhat larger and attributable to $HClO_4$.

In agreement with vapor density measurements (*5*), no Cl_2O_6 parent was seen at 10^{-7} torr, all of the oxide apparently being ClO_3. The oxide Cl_2O_7 showed a very small parent peak and a small ClO_4^+ fragment. This is to be compared with $HClO_4$, which gives no ClO_4^+ and a large parent. The Cl_2O_7 spectrum agrees very well with a spectrum of Fisher (*3*), which has appeared since this work was completed.

In the case of Cl_2O, there could be some question as to the source of the Cl_2^+ fragments. Both methods of preparation gave the same spectra, and after an initial Cl_2 and O_2 removal showed pattern coefficients constant in time and independent of sample temperature. It is concluded that Cl_2^+ is a real fragment from Cl_2O. The spectrum compares favorably with that of Freeman and Phillips (*4*), if one assumes a small amount of Cl_2 in their sample, perhaps due to decomposition, although no O_2 is reported by them. Their HCl peaks are large and may account for some of the excess at 35, 37 as compared to this work. The Cl_2O spectrum of Fisher (*2*) shows slightly lower 70, 72, 74 peaks and may indicate a small amount of Cl_2 in our sample, or may merely represent the difference in mass spectrometers.

The general agreement between the spectra of different investigators indicates that the CO_2^+ observed in other work was probably not associated with reaction in the bulk of the material but rather came from carbonized filaments.

LITERATURE CITED

(1) Brauer, G., ed., "Handbook of Preparative Inorganic Chemistry" (English trans.), Vol. 1, pp. 272–320, Academic Press, New York, 1963.
(2) Fisher, I. P., *Trans. Faraday Soc.* **63**, 684 (1967).
(3) *Ibid.*, **64**, 1852 (1968).
(4) Freeman, C. G., Phillips, L. F., *J. Phys. Chem.* **72**, 3025 (1968).
(5) Goodeve, C. F., Todd, F. A., *Nature* **132**, 514 (1933).
(6) Heath, C. A., Majer, J. R., *Trans. Faraday Soc.* **60**, 1783 (1964).
(7) Schack, C. J., Lindahl, C. B., *Inorg. Nucl. Chem. Letters* **3**, 387 (1967).

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Reaction of Hydrogen with Praseodymium at Various Temperatures

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The reaction of praseodymium with hydrogen was investigated in the temperature region 100° to 800° C. The predominant portion of the hydrogen is taken up at a constant rate. The final saturation with hydrogen is diffusion-controlled and obeys the parabolic laws. A reaction mechanism is proposed in terms of the various phases of reaction displayed by plots of average composition vs. time.

THE LITERATURE of rare-earth hydrides is somewhat clouded by conflicting results, especially with regard to rates of reaction. Thus, while the thermodynamics and structures of the various hydrides have been adequately investigated (*1, 2*), little attention has been paid to the times required to reach equilibrium. The object of this investigation is therefore to elucidate some of the variables that govern the rate of hydrogen uptake of praseodymium, hopefully gaining some insight into the various steps involved in the reaction. Because of their great "storage" capacity for hydrogen per unit volume, rare-earth metal hydrides have been the subject of frequent investigations by workers in such diverse fields as electronics, preparative chemistry, vacuum technology, and others. The greatest incentive for studying rare-earth hydrides lies, however, in their contribution to the over-all understanding of the complex field of solid-gas reactions.

EXPERIMENTAL

Preparation of Metal Samples. The praseodymium used in this study was obtained from Lindsay Rare-Earth Chemicals, American Potash and Chemical Corp., West Chicago, Ill. Analyses were as follows:

Praseodymium:	99.9%, Lot LU06044	
Impurities:	Tantalum	0.001%
	Calcium	0.0015
	Magnesium	0.001
	Aluminum	0.0005
	Oxygen	0.005
	Nitrogen	0.005
	Molybdenum	0.005
	Other rare-earths	<0.1

Samples 4 × 6 × 2 mm. cut from ingots using a fine-tooth saw were filed smooth and then abraded under light mineral oil, with silicon carbide paper. They were then washed under acetone, weighed, and placed under vacuum in a reaction vessel that had previously been purged three times with hydrogen. All samples were annealed at 700° C. for 3 hours.

Hydrogen. Matheson Ultra Pure hydrogen (Analysis: oxygen 0.5 p.p.m., nitrogen less than 5.0 p.p.m., total hydrocarbons as CH_4 less than 0.3 p.p.m.) was passed through a trap of equal molar concentrations of sodium and potassium to remove trace impurities. Electrolytic grade hydrogen was used for Run 7 (Analysis: oxygen 20 p.p.m., nitrogen 50 p.p.m., carbon dioxide 5 p.p.m., CH_4 and CO "trace").

Apparatus. The reaction was carried out in a high-vacuum system of conventional design (pressure, 10^{-5} mm. of Hg). The 20-mm.-diameter quartz reaction tube was heated by means of a Hevi-Duty furnace. Temperature control was achieved with a Type 500 Temcometer. A chromel-alumel thermocouple placed against the outer wall of the quartz tube served as a sensing element. The Temcometer was calibrated against a platinum-platinum 10% rhodium thermocouple. The specimen in a porcelain boat was positioned in the approximate center of the quartz tube.

Procedure. With the annealed metal sample in position under vacuum, the reaction chamber was brought up to temperature. Hydrogen was then admitted to give the desired pressure and the timer actuated simultaneously. Manometer readings were made with a Gaertner cathetometer. A run was considered completed when no pressure change occurred over at least a 15-minute period. At the conclusion of a run, the furnace was turned off, and, in some cases, hydrogen uptake was allowed to proceed overnight at ambient temperature, thus yielding the room-temperature ratio of hydrogen

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