

Figure 2.—Plot of log k against  $(1/T) \times 10^3$  to determine the energy of activation in the reduction of neptunium(VI) with oxalic acid.

step is the formation of a hydrolyzed neptunium(VI)oxalic acid complex followed by the oxidation of the complex by additional  $NpO_2^{2+}$  ions. The assumptions are reasonable for at the acidity used in the runs the oxalate would have reacted as oxalic acid. That a complex is formed when oxalic acid is added to  $NpO_2^{2+}$ solution is supported by the color change, from the pink of Np(VI) to a marked yellow. For 4 equiv of  $NpO_2^{2+}$ ion to be reduced per mole of oxalate oxidized it would be necessary for oxygen to be oxidized to the element which probably occurs through the intermediate formation of a percarbonate. The following equations explain the stoichiometry and the orders observed with respect to reactants

$$NpO_2^{2^+} + H_2C_2O_4 + H_2O \xrightarrow{slow} NpO_2(OH)H_2C_2O_4^+ + H^+$$
 (1)  
fast

$$3NpO_2^{2+} + NpO_2(OH)H_2C_2O_4^+ \longrightarrow$$

$$H_1 D_2^2 + 2CO_2 + 5H^2 + 0.0O_2^2$$

$$NpO_2^2 + H_2C_2Q_4 + H_2O \longrightarrow$$

$$4NpO_2^+ + 2CO_2^- + 4H^+ + 0.5O_2^- (3)$$

1

211+ 1 0 50

(9)

Carbon dioxide was detected as a product of the reaction, but oxygen, while not detected, was included as a product in order to account for the stoichiometry and mechanism of the reaction. The oxygen produced was at such low concentration, of the order of  $10^{-8}$  Mfor complete reaction, that it would have been difficult to distinguish it from atmospheric oxygen although no runs free of atmospheric oxygen were attempted. Of course the product Np(V) was used in the analysis.

Contribution from Rocketdyne, a Division of North American Rockwell Corporation, Canoga Park, California 91304, and the Institut für Anorganische Chemie, Universität, Stuttgart, Germany

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# The Chloryl Cation, ClO<sub>2</sub>+

BY KARL O. CHRISTE, CARL J. SCHACK, DONALD PILIPOVICH, AND WOLFGANG SAWODNY

### Received April 30, 1969

The 1:1 adducts  $ClO_2F \cdot AsF_5$  and  $ClO_2F \cdot BF_8$  have been investigated. Whereas  $ClO_2F \cdot AsF_5$  is stable at ambient temperature, the  $ClO_2F \cdot BF_8$  adduct shows a dissociation pressure of 225 mm at 25°. A pressure-temperature curve gives a heat of reaction of 24.0 kcal mol<sup>-1</sup>, for the dissociation process:  $ClO_2F \cdot BF_3(s) = ClO_2F(g) + BF_3(g)$ . The X-ray powder patterns of  $ClO_2F \cdot AsF_5$  and  $ClF_8 \cdot AsF_5$  were recorded and indexed. Infrared and Raman measurements show that  $ClO_2F \cdot AsF_5$  and  $ClO_2F \cdot BF_3$  have the ionic structures  $ClO_2^+AsF_5^-$  and  $ClO_2^+BF_4^-$ , respectively, in the solid state. All fundamental vibrations were observed and a valence force field was calculated for  $ClO_2^+$ .

### Introduction

The existence of adducts between  $ClO_2F$  and Lewis acids such as  $SbF_5$ ,  $AsF_5$ ,  $BF_3$ ,  $PF_5$ ,  $VF_5$ ,  $SnF_4$ , etc., is well known and has been discussed in a review article.<sup>1a</sup> Ionic structures involving the  $ClO_2^+$  cation are generally assumed for these complexes.<sup>1a,b</sup> However, no experimental data have been reported to support this assumption. Since  $ClO_2F$  is the preferred product formed by the reaction of water,<sup>2</sup> oxides, or hydroxides with chlorine fluorides (independent of their oxidation state), it is the most common impurity in reactions involving any chlorine fluoride. Poorly passivated sections of metal vacuum lines or contact with glass is often sufficient to produce substantial amounts of  $ClO_2F$ . Thus, in reactions between chlorine fluorides and Lewis acids,  $ClO_2F$  is extremely difficult to remove from the

 <sup>(</sup>a) M. Schmeisser and K. Brändle, Advan. Inorg. Chem. Radiochem., 5, 41 (1963).
 (b) After submitting this paper for publication, we have learned about a paper by G. A. Carter, A. M. Qureshi, and F. Aubke, Chem. Commun., 1461 (1968), dealing with the existence of the ClO<sub>2</sub>+ cation in solution.

system due to the relatively high stability of its Lewis acid adducts. Hence, a better characterization of the  $ClO_2F$ ·(Lewis acid) adducts seemed very desirable. In this paper we wish to report the data obtained for the 1:1 adducts  $ClO_2F$ ·AsF<sub>5</sub> and  $ClO_2F$ ·BF<sub>3</sub>.

## **Experimental Section**

Materials and Apparatus.—The materials used in this work were manipulated in a well-passivated (with  $ClF_{\delta}$ ) 304 stainless steel vacuum line equipped with Teflon FEP U traps and 316 stainless steel bellows-seal valves (Hoke Inc., 4251F4V). Arsenic pentafluoride (from Ozark Mahoning Co.) and BF<sub>3</sub> (from The Matheson Co., Inc.) were purified by several low-temperature vacuum distillations. Chloryl fluoride (prepared in this laboratory from KClO<sub>3</sub> and F<sub>3</sub><sup>3</sup>) was purified by fractional condensation. The purity of the starting materials was determined by measurements of their vapor pressures and infrared spectra. Because of their hygroscopic nature, materials were handled outside of the vacuum system in the dry nitrogen atmosphere of a glove box.

Preparation of the Adducts.  $\text{ClO}_2^+\text{AsF}_6^-$ .—In a typical experiment  $\text{ClO}_2\text{F}$  (11.7 mmol) and  $\text{AsF}_5$  (10.4 mmol) were combined at  $-196^\circ$  in a passivated reactor constructed from Kel-F and stainless steel. The mixture was allowed to warm up slowly until melting and reaction occurred. The initial pressure rise was followed by a decrease as a white, solid complex formed. After keeping the mixture at 23° for 30 min, unreacted ClO<sub>2</sub>F (1.5 mmol) was removed *in vacuo* and identified by its infrared spectrum. Therefore, ClO<sub>2</sub>F (10.2 mmol) had reacted with AsF<sub>5</sub> (10.4 mmol) in a mole ratio of 1:1.02 producing the complex  $\text{ClO}_2^+\text{AsF}_6^-$ .

 $ClO_{2}+BF_{4}-$ .—Chloryl fluoride (1.88 mmol) and BF<sub>3</sub> (2.86 mmol) were combined at  $-196^{\circ}$  in a passivated Teflon FEP U trap. The mixture was allowed to warm up slowly until melting and reaction occurred. After cycling the temperature several times between  $-196^{\circ}$  and a temperature at which the pressure inside the U trap reached 1500 mm, unreacted BF<sub>3</sub> (0.94 mmol) was removed at  $-78^{\circ}$  by vacuum distillation and identified by its infrared spectrum. Hence,  $ClO_2F$  (1.88 mmol) had reacted with BF<sub>3</sub> (1.92 mmol) in a mole ratio of 1:1.02 producing the complex  $ClO_2+BF_4-$ .

 $\textbf{ClF}_2\textbf{+}\textbf{AsF}_6\textbf{-}\textbf{.}$  The preparation of this complex has previously been described.<sup>4</sup>

Dissociation Pressure Measurements.—The  $\text{ClO}_2^+\text{BF}_4^-$  complex was prepared in a Teflon FEP container directly connected to a Heise Bourdon tube-type gauge (0–1500 mm ±0.1%). The temperature of the cooling bath was determined with a copper-constantan thermocouple. To be certain that an equilibrium existed at each temperature reading, a sample of the gas above the solid complex was pumped off and a constant pressure was reestablished. True equilibrium existed at a given temperature if the pressures, before and after the pumping off procedure, were identical. Equilibrium pressures were always approached from below a given temperature. The following temperatures (°C) and vapor pressures (mm) were observed: -23.3, 4.5; -11.6, 13; 0.0, 35; 7.2, 62; 13.2, 98; 15.0, 112; 22.1, 182. The best fit of log *P vs. T*<sup>-1</sup> (in °K<sup>-1</sup>) was obtained by the method of least squares.

X-Ray Powder Data.—Debeye-Scherrer powder patterns were taken using a Philips Norelco instrument, Type No. 12046, with copper K $\alpha$  radiation and a nickel filter. Samples were sealed in Lindemann glass tubes ( $\sim 0.3$ - and  $\sim 0.5$ -mm o.d.).

Vibrational Spectra.—The infrared spectra were recorded on Beckman Models IR-9 and IR-7 (with CsI interchange) and a Perkin-Elmer Model 337 spectrophotometer in the ranges 4000-400, 700-250, and 4000-400 cm<sup>-1</sup>, respectively. The instruments were calibrated by comparison with standard gas calibration points.<sup>5</sup> The spectra of gases were obtained using 304 stainless steel cells of 5-cm path length fitted with AgCl windows. Screw-cap metal cells with AgCl plates or very thin Teflon FEP sheet were used for obtaining the spectra of solids as dry powders. The low-temperature spectra were taken by preparing the complex on the internal window (cooled with liquid nitrogen) of an infrared cell. Unreacted starting materials were removed *in vacuo* by allowing the internal window to warm up shortly. The body of the low-temperature cell was made from Pyrex glass, all windows being AgCl.

The Raman spectra were recorded using a Spectra Physics Model 125 He–Ne laser as a source of  $\sim 80$  mW of exciting light at 6328 Å and a Baird Type 1310 interference filter (45 Å halfwidth). The scattered light was analyzed with a Spex Model 1400 double monochromator, a photomultiplier cooled to  $\sim -25^{\circ}$ , and a d.c. ammeter. Neon lines were used for calibration and the frequency accuracy was 1 cm<sup>-1</sup> or better throughout the region covered. Pyrex-glass tubes (7-mm o.d.) with a hollow inside glass cone for variable sample thickness were used as sample containers.

#### **Results and Discussion**

Synthesis and Properties.—Chloryl fluoride and  $AsF_5$  when combined produced the 1:1 complex,  $ClO_2+AsF_6-$ , a white crystalline solid. The 1:1 combining ratio was established by quantitative synthesis. The  $ClO_2+AsF_6-$  complex has no measurable dissociation pressure at room temperature and reacts explosively with water. These data are in good agreement with those previously reported.<sup>1a,6-3</sup>

Similarly, BF<sub>3</sub> and ClO<sub>2</sub>F reacted in a 1:1 mole ratio to form the white, crystalline adduct  $ClO_2^+BF_4^-$ . This adduct is not stable at ambient temperature. Based on the observed dissociation pressure-temperature data, a plot of log  $P_{mm}$  vs.  $T^{-1}$  (in °K<sup>-1</sup>) for the heterogeneous equilibrium

$$ClO_2^+BF_4^-(s) = ClO_2F(g) + BF_3(g)$$

is a straight line. The equation log  $P_{\rm mm} = 11.1482 - (2623.1/T)$  represents these data in the temperature range -23 to  $22^{\circ}$ . The standard error of the estimate of log P was 0.003 which corresponds to 0.7% deviation in pressure. The index of correlation ( $\rho$ ) is 0.999978. By extrapolation, a dissociation pressure of 1 atm was obtained at 44.1°. At 25° the dissociation pressure amounts to 225 mm. From the slope of the log  $P_{\rm mm}$  vs.  $T^{-1}$  curve,  $\Delta H_{\rm d}^{\circ 9} = 24.01$  kcal mol<sup>-1</sup> was found. From  $\Delta F^{\circ}{}_T = -RT \ln K\rho(\text{atm})$ , a free energy change,  $\Delta F^{\circ}{}_{298} = 2.264$  kcal mol<sup>-1</sup>, and from  $\Delta S^{\circ}{}_T = (\Delta H^{\circ} - \Delta F^{\circ}{}_T)T^{-1}$ , an entropy change,  $\Delta S^{\circ}{}_{298} = 72.92$  cal deg<sup>-1</sup> mol<sup>-1</sup>, were found for the dissociation process at 25°. A heat of formation of  $\text{ClO}_2+\text{BF}_4-(\text{s})$ ,  $\Delta H_{\rm f}^{\circ}{}_{298} = -303$  kcal mol<sup>-1</sup>, was calculated based upon  $\Delta H_{\rm f}^{\circ}{}_{298}[\text{ClO}_2-$ 

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 $F(g)^{10} = -7$  kcal mol<sup>-1</sup> and  $\Delta H_f^{\circ}_{298}[BF_3(g)]^{11} =$ -271.65 kcal mol<sup>-1</sup>. The uncertainty in the heat of formation value of  $ClO_2^+BF_4^-$  is mainly due to the uncertainty in the value of the heat of formation of  $ClO_2F$ . The heat of dissociation,<sup>9</sup> 24.01 kcal mol<sup>-1</sup>, obtained for  $ClO_2+BF_4$  is very close to the value of 23.6 kcal mol<sup>-1</sup> found<sup>12</sup> for the similar complex CIF<sub>2</sub>+- $BF_4^-$ . This is not surprising since both adducts are ionic and have comparable stability, and their cations are of similar size and geometry.13

X-Ray Powder Data.-Table I lists calculated and observed X-ray powder diffraction data (indexed in the tetragonal system) for ClO<sub>2</sub>+AsF<sub>6</sub><sup>-</sup>. From these data, the calculated unit cell dimensions are a = 10.39 and c= 8.03 Å. Assuming that the volume of the oxygen atoms will be comparable to that of the fluorine atoms, and neglecting contributions from the highly charged central atoms to the volume (as suggested by Zachariasen<sup>14,15</sup>), an average volume of 17 to 18 Å<sup>3</sup> can be expected for each fluorine or oxygen atom in ClO<sub>2</sub>+- $AsF_6$ <sup>-</sup>. Thus, values of 17.8 and 17.0 Å<sup>3</sup> have been reported for IF<sub>6</sub>+AsF<sub>6</sub>- <sup>16</sup> and NF<sub>4</sub>+AsF<sub>6</sub>-,<sup>17,18</sup> respectively. Based on this assumption, one can deduce six molecules per unit cell for  $ClO_2^+AsF_6^-$  resulting in an average volume of 18.05 Å<sup>3</sup> per F or O atom.

Since the  $ClO_2^+$  and the  $ClF_2^+$  cations might be expected to be similar in size and geometry, we have also recorded and indexed the powder pattern for CIF2+- $AsF_6^-$  (see Table I). The unit cell was found to be tetragonal with a = 7.48 and c = 10.20 Å. Assuming four molecules per unit cell, an average volume per F atom of 17.8 Å<sup>3</sup> was calculated. The crystal structure of  $ClF_2^+AsF_6^-$  can be considered as a tetragonally distorted face-centered-cubic cell which is guite common for  $R(MX_6)$ -type compounds.<sup>19</sup> The fact that the observed powder patterns and calculated unit cell dimensions differ considerably for ClF2+AsF6- and  $ClO_2$  +AsF<sub>6</sub> - might be due to the different bond angles (estimated to be 95 and 120°, respectively) of the two cations.

Vibrational Spectra.—Figures 1 and 2 show the Raman and infrared spectra, respectively, of solid  $ClO_2$ +AsF<sub>6</sub>-. No absorption bands were observed in the infrared spectrum below  $400 \text{ cm}^{-1}$ . The 1296- and 1044-cm<sup>-1</sup> bands were recorded under high-resolution conditions for both the dry powder sample at ambient temperature and the low-temperature sample to measure the <sup>35</sup>Cl-<sup>37</sup>Cl isotope splitting. Ten measurements were made for each band pair resulting in an average

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			TABLE	εI			
X-Ray	POWDER	r Data	FOR Cl	O <sub>2</sub> +AsF <sub>6</sub> -	· and Cl	F <sub>2</sub> +AsF	`6 <sup></sup>
	$C1O_2^+A$	.sF6-	ClF2+AsF6-				
$\overline{}^{d}$ ,	Å	<b>.</b> .		d,	Å	•	
Obsd	Calcd	Intens	nkl	Obsd	Caled	Intens	hkl
7.50	7.34	m	110	5.94	6.03	w	101
5.55	5.49	m	111	5.34	5.28	S	110
5.10	5.19	m	200	4.84	4.70	w	111
4,40	4.36	s	201	4.67)		w	
4.02	4.02	m	$002 \\ 211$	4.21	4.21	vs	102
				3.81)	2 74	w	200
3.65	3.67	vs	220	3.72)	0.74	m	200
3.57	3.52	vs	112	3.34	3.34	vw	210
3.49	3.46	w	300	3.21	3.18	m	211
3.03	3.04	ms	311				
2.87	2.88	w	320	3.02	3.02	w	202
2.76		w		2.75		vw	
2.69	2.68	w	003	2.66	2.64	vw	220
2.54	2.51	w	410	2.54	2.55	vw	004
2.30	2.32	w	420	2.49	2.49	w	300
2.16	2.16	vw	223	2.42	2.42	vw	301
2.08	2.08	s	500	2.29	2.30	vw	311
2.05	2.04	s	510	2.102	2.107	vw	204
2.013	2.011	vw	{004	2.070	2.075	w	320
			(501	2.013	2.011	vw	303
1.955	1.963	ms	323	1.826	1.814	w	410
1.857		w		1.786	1.789	w	411
1.836		w		1.663	1.673	vw	420
1.796		w					
1.757		W		1.627	1.638	vw	403
1.723		vw					
1.697		mw					
1.660		vw					
1.586		mw					
1.548		w					
1.522		w					



Figure 1.-Raman spectrum of solid ClO<sub>2</sub>+AsF<sub>6</sub>-. A indicates spectral slit width.



Figure 2.—Infrared spectrum of solid  $ClO_2^+AsF_6^-$  as dry powder at ambient temperature (B) and as a film at low temperature (A).

frequency-difference value of  $13.80 \pm 0.19 \text{ cm}^{-1}$  for  $\nu_3$  (B<sub>1</sub>) and of 5.40  $\pm$  0.07 cm<sup>-1</sup> for  $\nu_1$  (A<sub>1</sub>). The uncertainty is mainly due to the difficulty in accurately locating the band center. The  $\nu_2$  (A<sub>1</sub>) band pair could

1	ABLE 11
Vibrational Spectra of $ClO_2$ +AsF <sub>6</sub> <sup>-</sup> and $ClO_2$ +BF	$_4^-$ and Their Assignments Compared with Those of $\mathrm{SO}_2^-$
	Assignment (point group)

Obsd freq, cm <sup>-1</sup>				Assignment (point group)			
C1O <sub>2</sub> +	AsF6	C1O <sub>2</sub> +BF <sub>4</sub> -	$SO_2^a$	$XO_2 (C_{2v})$	$AsF_{6}$ (O <sub>h</sub> )	$BF_4^-(T_d)$	
$ \begin{array}{c} 1296.4 m \\ 1282 6 mw \end{array} $	1296.4(1)	1308 m 1294 mw	1362 vs	$\nu_3$ (B <sub>1</sub> )		$ u_1 +  u_4 (F_2) $	
1043.7 mw( 1038.3 w ∫	1044.4(10) 1039.1(4)	1100–990 vs	1151 ms	$\nu_1~({\rm A}_1)$		$\nu_{8}$ (F <sub>2</sub> )	
825 vw		772 mw			$\nu_2 + \nu_6 (F_{1u} + F_{2u})$		
694 vs 680 m 569 mw	$684 (8) \\570 (5)$				$egin{array}{lll}  u_3 & ({f F}_{1u}) \  u_1 & ({f A}_{1g}) \  u_2 & ({f E}_g) \end{array}$	$\nu_1$ (A <sub>1</sub> )	
		532 w, sh				$\nu_4 (F_2) {}^{10}B$	
521.0 m 517 sh	521.3 (3)	521 mw, sh 518 m	518 m	$\nu_2$ (A <sub>1</sub> )	$p_4$ (F <sub>10</sub> )	$ u_4 (\mathbf{F}_2) \ ^{11}\mathbf{B}$	
400 s							
	372 (5)				$\nu_5 (\mathrm{F}_{2\mathrm{g}})$		
<sup>a</sup> See ref 18.							



Figure 3.—Low-temperature infrared spectrum of solid  $ClO_2^+-BF_4^-$ .

not be resolved sufficiently to allow a very precise determination of the isotope splitting. Figure 3 shows the low-temperature infrared spectrum of  $ClO_2^+BF_4^-$ . The observed frequencies of the vibrational spectra are listed in Table II. For comparison the frequencies reported<sup>20</sup> for SO<sub>2</sub>, which is isoelectronic with  $ClO_2^+$ , are also included. The absence of solid  $ClO_2F^{21}$  and  $AsF_5^4$  or  $BF_{3,}^{22}$  respectively, in the low-temperature infrared spectra is readily established by comparison with the spectra of the pure, solid starting materials.

The simplicity of the observed spectra and the occurrence of the bands characteristic for  $AsF_6^-$  and  $BF_4^-$  show that the  $ClO_2F \cdot AsF_5$  and  $ClO_2F \cdot BF_3$  adducts must have the ionic structures,  $ClO_2^+AsF_6^-$  and  $ClO_2^+BF_4^-$ , respectively. Since the vibrational spectra of the anions  $AsF_6^-$  and  $BF_4^-$  are well known, they will be discussed first.

An octahedral ion, such as  $AsF_6^-$ , has  $O_h$  symmetry. The six normal modes of vibration are classified as  $A_{1g} + E_g + 2 F_{1u} + F_{2g} + F_{2u}$ . Of these only the two  $F_{1u}$  modes will be infrared active, while only the  $A_{1g}$ ,  $E_g$ , and  $F_{2g}$  modes will be Raman active, assuming that the selection rules are valid and the octahedron is not distorted. The remaining  $F_{2u}$  mode is inactive in both the infrared and Raman spectra. For  $ClO_2^+AsF_6^-$  all five fundamental vibrations belonging to  $AsF_6^-$  were observed, the observed frequencies and intensities being similar to those of other  $AsF_6^-$ -containing complexes such as  $ClF_2^+AsF_6^-$ ,<sup>13</sup>  $NF_4^+AsF_6^-$ ,<sup>23</sup>  $NF_2O^+AsF_6^-$ ,<sup>24</sup> and  $IF_6^+AsF_6^-$ .<sup>16</sup> The only deviations from the selection rules were observed for  $\nu_2$  ( $E_g$ ) and  $\nu_1$  ( $A_{1g}$ ). These two modes should be only Raman active but were also observed in the infrared spectrum. This breakdown of the selection rules has also been observed for the infrared spectra of most of the other  $AsF_6^-$ -containing salts.<sup>13,16,23,24</sup> It could be due to slight distortion of the  $AsF_6^-$  octahedron or crystal field effects.<sup>13</sup>

A tetrahedral ion, such as  $\rm BF_4^-$ , has  $\rm T_d$  symmetry. The four normal modes of vibration are classified as  $\rm A_1 + E + 2~F_2$ . Of these, all four modes are expected to be Raman active whereas only the two  $\rm F_2$  modes should be infrared active. However, crystal field effects or slight distortion of the  $\rm BF_4^-$  tetrahedron can result in the  $\rm A_1$  mode also becoming infrared active. For  $\rm ClO_2^+BF_4^-$  all bands expected for  $\rm BF_4^-$  were observed and assigned by analogy with the known spectra of  $\rm K^+BF_4^{-,25-27}$   $\rm ClF_2^+BF_4^{-,13}$  and  $\rm FCl_2^{+-}BF_4^{-,28}$ 

The three remaining band pairs observed in the spectra of both  $\text{ClO}_2^+\text{AsF}_6^-$  and  $\text{ClO}_2^+\text{BF}_4^-$  complexes should be due to  $\text{ClO}_2^+$ . A symmetric triatomic ion of the type  $\text{XO}_2^+$ , such as  $\text{ClO}_2^+$ , could be either linear or bent. Linear  $\text{XO}_2^+$  has symmetry  $D_{\text{csh}}$ . The three normal modes of vibration are classified as  $\Sigma_g^+ + \Pi_u + \Sigma_u^+$ . Since linear  $\text{XO}_2^+$  has a symmetry center, it follows the rule of mutual exclusion. Therefore, only  $\Pi_u$  and  $\Sigma_u^+$  will be infrared active. Bent  $\text{XO}_2^+$  has symmetry  $\text{C}_{2v}$ . The three normal modes of vibration

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are classified as 2  $A_1 + B_1$ . All three modes will be infrared and Raman active. Furthermore, the frequency difference between  $\nu_1$  and  $\nu_3$  should be much larger for linear XY<sub>2</sub> than for bent XY<sub>2</sub>. Since for ClO<sub>2</sub><sup>+</sup> three bands were observed in both the infrared and Raman spectra showing a frequency difference of only 250 cm<sup>-1</sup> for the two stretching vibrations, the possibility of symmetry  $D_{\infty h}$  is eliminated. This is not surprising since ClO<sub>2</sub><sup>+</sup> has one nonbonded pair of electrons which is expected to be sterically active.

The observed vibrational spectra might also be interpreted in terms of an asymmetric  $ClO_2^+$  cation, since it would also show three active vibrations in both the infrared and Raman spectra. An asymmetric, linear  $ClO_2^+$  cation, however, does not seem likely, since one would expect a much larger frequency difference between  $\nu_1$  and  $\nu_3$  and since isoelectronic SO<sub>2</sub> is known to be a symmetric bent molecule and exhibits an infrared spectrum<sup>20</sup> very similar to that of  $ClO_2^+$  (see Table II). However, slight distortion of bent ClO<sub>2</sub>+ (possibly due to crystal field effects) cannot be ruled out. Consequently, assignments for  $ClO_2^+$  were made for point group  $C_{2v}$  by analogy with isoelectronic SO<sub>2</sub>. All three bands of  $ClO_2^+$  show a splitting into two bands each. The observed frequency differences and relative intensities of the bands suggest that the splitting is due to the <sup>35</sup>Cl and <sup>37</sup>Cl isotopes. The bands belonging to <sup>37</sup>Cl have the lower frequencies and lower relative intensities. The fact that  $\nu_1$  (A<sub>1</sub>) shows a pronounced isotope splitting also eliminates a linear structure of symmetry D<sub>wh</sub>.

The  $\text{ClO}_2^+$  deformation vibration occurs in the same range as some of the  $\text{ClF}_x$  deformation vibrations. Furthermore,  $\text{AsF}_6^-$  and  $\text{BF}_4^-$  have a combination vibration,  $(\nu_2 + \nu_3)$  and  $(\nu_1 + \nu_4)$ , respectively, at frequencies close to that of  $\nu_3$  (B<sub>1</sub>) of  $\text{ClO}_2^+$ . Consequently, detection of small amounts of  $\text{ClO}_2^+\text{AsF}_6^-$  or  $\text{ClO}_2^+\text{BF}_4^-$  in the presence of  $\text{ClF}_x^+\text{AsF}_6^-$  or  $\text{ClF}_x^+$ - $\text{BF}_4^-$ , respectively, is difficult. Thus, some of the lowtemperature infrared spectra reported previously<sup>13,28</sup> may have contained small amounts of  $\text{ClO}_2^+$  containing salts. Distinction between  $\nu_3$  (B<sub>1</sub>) of  $\text{ClO}_2^+$  and  $(\nu_2 + \nu_3)$  of  $\text{AsF}_6^-$  can be made based upon their different band shapes. Both bands have a doublet structure; however, their relative intensities are reversed.

Force Constants.—The knowledge of the exact  ${}^{35}\text{Cl}{}^{-37}\text{Cl}$  isotope shifts for the two stretching vibrations and of an approximate value for the deformation vibration might allow the calculation of a general valence force field (GVFF) for ClO<sub>2</sub><sup>+</sup>. However, the geometry of ClO<sub>2</sub><sup>+</sup> is not known. Whereas the Cl–O bond distance cancels out if the deformation constant is expressed in mdynes per ångström, the influence of the O–Cl–O bond angle on the force constants cannot be neglected. The Teller–Redlich product rule might be used for the calculation of the bond angle.<sup>29</sup> For ClO<sub>2</sub><sup>+</sup>

only the  $B_1$  vibration can be used since those of species  $A_1$  are angle independent. There is only one mode in species  $B_1$ , and, hence, the following direct relationship applies where the primed values belong to the  ${}^{37}Cl$  isotope

$$\cos \alpha = 1 - \frac{\nu'_{3}^{2} - \nu_{3}^{2}}{m_{0} \left(\frac{\nu'_{3}^{2}}{m_{Cl}} - \frac{\nu_{3}^{2}}{m'_{Cl}}\right)}$$

Based on this relationship and the observed frequencies, an O-Cl-O bond angle of  $114.0^{\circ}$  is calculated for  $ClO_2^+$ . However, this value appears low since bond angles of 110.5 and 117.6° were reported<sup>30</sup> for  $ClO_2^-$  and  $ClO_2$ , respectively. For  $ClO_2^+$  a further angle increase is likely and a value of  $120^{\circ}$  can be expected by analogy with the value of  $119^{\circ}$  reported<sup>30</sup> for isoelectronic SO<sub>2</sub>. However, an increase of  $\Delta \nu_{3}$  by 0.5 cm<sup>-1</sup> would result in an angle of 120°. Such a small change in  $\Delta v_3$  could be caused by anharmonicity effects. Hence, even very accurate frequency values will not be sufficient for a reliable angle determination as long as no anharmonicity corrections are available. Based on these considerations, the calculated value of 114° might be taken as the lower limit and a value between 120 and 125° as the upper limit for the bond angle of  $ClO_2^+$ .

Owing to the uncertainty of the bond angle, a GVFF was calculated for  $ClO_2^+$  from the isotopic frequencies assuming bond angles of 105, 110, 115, 120, and 125°. For the B<sub>1</sub> vibration, two separate sets of  $F_{33}$  were calculated using the <sup>35</sup>ClO<sub>2</sub><sup>+</sup> and <sup>37</sup>ClO<sub>2</sub><sup>+</sup> frequencies, respectively. Table III shows the arithmetic mean of the two sets with a variance of  $\pm 0.01 \text{ mdyn/Å}$  covering both the <sup>35</sup>ClO<sub>2</sub><sup>+</sup> and <sup>37</sup>ClO<sub>2</sub><sup>+</sup> values for all angles. For species A<sub>1</sub> two sets of symmetry force constants were calculated based on the observed infrared and Raman frequencies, respectively. Table III shows the mean values and their variance. For the computation of the A<sub>1</sub> force field, only the intersection point of the  $F_{11}/F_{12}$  ellipses for <sup>35</sup>ClO<sub>2</sub><sup>+</sup> and <sup>37</sup>ClO<sub>2</sub><sup>+</sup> was used since  $\Delta\nu_2$  is not known with sufficient accuracy.

Table III shows that the valence force constant,  $f_{\rm r}$ , and the deformation constant,  $f_{\alpha}$ , exhibit only a slight bond angle dependence and have values of  $8.96 \pm 0.06$ and  $0.82 \pm 0.03$  mdyn/Å, respectively, for the angle range 115–125°. However, the two interaction constants  $f_{\rm rr}$  and  $f_{\rm r\alpha}$  depend strongly on the bond angle and, hence, cannot be determined exactly. For the bond angle range 115–125°,  $f_{\rm rr}$  and  $f_{\rm r\alpha}$  have values of  $-0.45 \pm$ 0.13 and 0.24  $\pm$  0.13 mdyn/Å, respectively.

Table IV shows a comparison between the force constants of  $ClO_2^+$  and those of related species. For  $ClO_2^-$  the listed force constants have been calculated<sup>30</sup> using an approximating method<sup>31</sup> which for the related  $ClO_2$  radical resulted in values<sup>32</sup> very close to those<sup>33</sup> of a

<sup>(29) (</sup>a) W. Sawodny and K. Ballein, to be submitted for publication. (b) After submitting this paper for publication, we have learned that J. W. Hastie, R. Hauge, and J. L. Margrave, J. Inorg. Nucl. Chem., **31**, 281 (1969), have used the same relation to determine the bond angles in SO<sub>2</sub> and SeO<sub>2</sub> from isotopic frequencies.

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<sup>(33)</sup> M. G. Krishna Pillai and R. F. Curl, Jr., J. Chem. Phys., 37, 2921 (1962).

TABLE III FORCE CONSTANTS (MDYN/Å) OF  $ClO_2^+$  (Assuming Different Bond Angles)

Bond angle,	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	Symmetry	force constants		Internal force constants		
deg	$F_{11} = f_{\rm r} + f_{\rm rr}$	$F_{12} = \sqrt{2}f_{r\alpha}$	$F_{22} = f_{\alpha}$	$F_{83} = f_r - f_{rr}$	$f_{\mathbf{r}}$	frr	
105	$8.27 \pm 0.03$	$0.97 \pm 0.03$	$0.94\pm0.01$	$10.04\pm0.01$	$9.16 \pm 0.01$	$-0.89 \pm 0.02$	
110	$8.36\pm0.02$	$0.75\pm0.02$	$0.89 \pm 0$	$9.81 \pm 0$	$9.09 \pm 0.01$	$-0.73 \pm 0.01$	
115	$8.44 \pm 0.02$	$0.54 \pm 0.01$	$0.85 \pm 0$	$9.60 \pm 0.01$	$9.02 \pm 0.01$	$-0.58\pm0.02$	
120	$8.51\pm0.02$	$0.35\pm0.01$	$0.82\pm 0$	$9.40 \pm 0.01$	$8.96 \pm 0.01$	$-0.45\pm0.02$	
125	$8.57\pm0.01$	$0.16\pm0.01$	$0.80\pm0$	$9.22 \pm 0.01$	$8.90 \pm 0$	$-0.33\pm0.01$	

GVFF. The data listed for  $ClO_2$  and  $SO_2$  are GVFF values computed with the aid of centrifugal distortion constants,<sup>33,34</sup> which for SO<sub>2</sub> are almost identical with the GVFF values computed from isotopic shifts.<sup>35</sup> As can be seen from Table IV, there is a substantial increase of the valence force constant,  $f_r$ , for the sequence  $ClO_2^-$ ,  $ClO_2$ ,  $ClO_2^+$ . This increase of  $f_r$  is mainly due to the increase in the formal bond order value from 1.5 in  $ClO_2^-$  to 2 in  $ClO_2^+$ . However, the observed increase is larger than expected for this effect alone. It could be explained by the increasing positive charge on the chlorine central atom<sup>36</sup> and an increasing s character of the chlorine orbitals involved in the  $\sigma$  bonds, changing from mainly sp<sup>3</sup> in  $ClO_2^-$  to sp<sup>2</sup> in  $ClO_2^+$ . The latter effect is also reflected by the increase in the bond angle from  $ClO_2^-$  toward  $ClO_2^+$  (see above). Comparison between the  $f_r$  value of  $ClO_2^+$  and that of  $SO_2$  does not show the increase one might predict based upon the increasing oxidation state of the central atom, but shows a marked decrease. Similar observations have been made for other isoelectronic pairs, such as CF<sub>4</sub>- $NF_4^{+\ 23}$  and  $OCl_2$ - $FCl_2^{+}$ ,<sup>28</sup> and have been attributed<sup>23,28</sup> to increasing bond polarity. It is difficult to rationalize the relatively high negative value of  $f_{\rm rr}$  for ClO<sub>2</sub><sup>+</sup>. However, similar negative values were found for  $f_{rr}$  of ClO<sub>2</sub>F<sup>37</sup> and ClO<sub>3</sub>F.<sup>31</sup>

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It should be interesting to compare  $\text{ClO}_2^+$  with  $\text{ClO}_2\text{F}$ . Smith, Begun, and Fletcher have reported<sup>37</sup> a modified valence force field for  $\text{ClO}_2\text{F}$  using isotopic frequencies for the computation of the important interaction constants. They found a very low value for the Cl–F valence force constant indicative of a highly polar Cl–F bond. Hence, the ClO<sub>2</sub> part in  $O_2\text{Cl}^{\delta+}-\text{F}^{\delta-}$  should be very similar to  $\text{ClO}_2^+$ . Indeed the agreement between the values found for  $\text{ClO}_2^+$  and those reported for  $\text{ClO}_2\text{F}$  ( $f_r = 9.07, f_{rr} = -0.12, f_{r\alpha} = 0.38$ , and  $f_{\alpha} = 1.06 \text{ mdyn}/\text{Å}^{37}$ ) is surprisingly good.

Acknowledgment.—This research was supported by the Office of Naval Research, Power Branch. The authors are indebted to Dr. J. P. McTague of the Science Center of North American Rockwell Corp. for the use of the Raman spectrophotometer. Helpful discussions with Dr. D. Lind of the Science Center and Dr. E. C. Curtis of Rocketdyne were greatly appreciated.