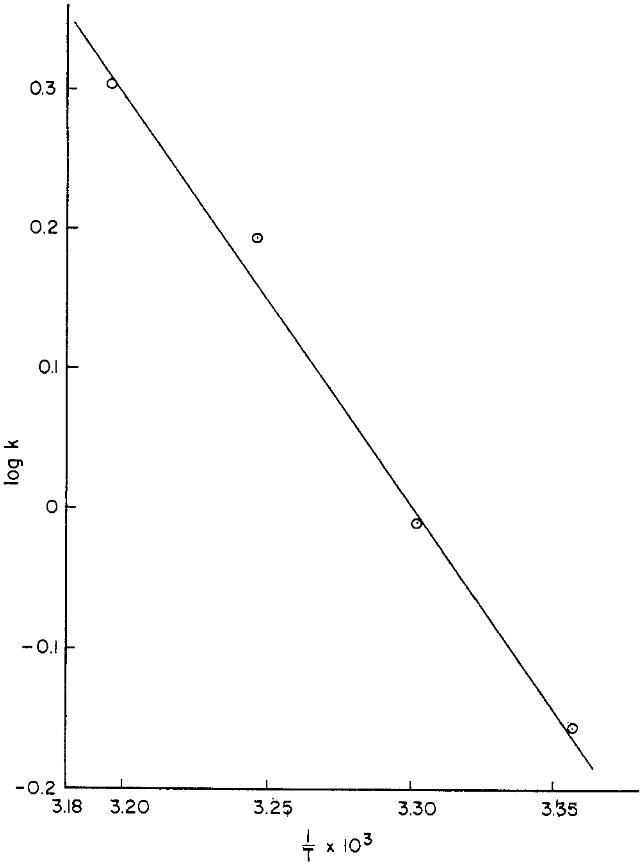

Figure 2.—Plot of log k against $(1/T) \times 10^3$ to determine the energy of activation in the reduction of neptunium(VI) with oxalic acid.

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

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

$$3NpO_2^{2+} + NpO_2(OH)H_2C_2O_4^+ \xrightarrow{\text{fast}} 4NpO_2^+ + 2CO_2 + 3H^+ + 0.5O_2 \quad (2)$$

$$4NpO_2^{2+} + H_2C_2O_4 + H_2O \longrightarrow 4NpO_2^+ + 2CO_2 + 4H^+ + 0.5O_2 \quad (3)$$

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^{-3} *M* for 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,
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The Chloryl Cation, ClO_2^+

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Received April 30, 1969

The 1:1 adducts $ClO_2F \cdot AsF_5$ and $ClO_2F \cdot BF_3$ have been investigated. Whereas $ClO_2F \cdot AsF_5$ is stable at ambient temperature, the $ClO_2F \cdot BF_3$ adduct shows a dissociation pressure of 225 mm at 25°. A pressure–temperature curve gives a heat of reaction of 24.0 kcal mol^{-1}, for the dissociation process: $ClO_2F \cdot BF_3(s) = ClO_2F(g) + BF_3(g)$. The X-ray powder patterns of $ClO_2F \cdot AsF_6$ and $ClF_3 \cdot AsF_5$ 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 $ClO_2^+AsF_6^-$ 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.[1a] Ionic structures involving the ClO_2^+ cation are generally assumed for these complexes.[1a,b] However, no experimental data have been reported to support this assumption. Since ClO_2F is the preferred product formed by the reaction of water,[2] 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

(1) (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_2^+ cation in solution.

(2) R. Bougon, M. Carles, and J. Aubert, *Compt. Rend.*, **266**, 179 (1967).

system due to the relatively high stability of its Lewis acid adducts. Hence, a better characterization of the $ClO_2F\cdot$(Lewis acid) adducts seemed very desirable. In this paper we wish to report the data obtained for the 1:1 adducts $ClO_2F\cdot AsF_5$ and $ClO_2F\cdot BF_3$.

Experimental Section

Materials and Apparatus.—The materials used in this work were manipulated in a well-passivated (with ClF_3) 304 stainless steel vacuum line equipped with Teflon FEP U traps and 316 stainless steel bellows-seal valves (Hoke Inc., 4251F4Y). Arsenic pentafluoride (from Ozark Mahoning Co.) and BF_3 (from The Matheson Co., Inc.) were purified by several low-temperature vacuum distillations. Chloryl fluoride (prepared in this laboratory from $KClO_3$ and F_2[3]) 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. $ClO_2^+AsF_6^-$.—In a typical experiment ClO_2F (11.7 mmol) and AsF_5 (10.4 mmol) were combined at −196° 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_2F (1.5 mmol) was removed *in vacuo* and identified by its infrared spectrum. Therefore, ClO_2F (10.2 mmol) had reacted with AsF_5 (10.4 mmol) in a mole ratio of 1:1.02 producing the complex $ClO_2^+AsF_6^-$.

$ClO_2^+BF_4^-$.—Chloryl fluoride (1.88 mmol) and BF_3 (2.86 mmol) were combined at −196° 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° and a temperature at which the pressure inside the U trap reached 1500 mm, unreacted BF_3 (0.94 mmol) was removed at −78° by vacuum distillation and identified by its infrared spectrum. Hence, ClO_2F (1.88 mmol) had reacted with BF_3 (1.92 mmol) in a mole ratio of 1:1.02 producing the complex $ClO_2^+BF_4^-$.

$ClF_2^+AsF_6^-$.—The preparation of this complex has previously been described.[4]

Dissociation Pressure Measurements.—The $ClO_2^+BF_4^-$ 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^{-1} (in °K^{-1}) 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 Kα radiation and a nickel filter. Samples were sealed in Lindemann glass tubes (~0.3- and ~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^{-1}, respectively. The instruments were calibrated by comparison with standard gas calibration points.[5] 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 ~80 mW of exciting light at 6328 Å and a Baird Type 1310 interference filter (45 Å half-width). The scattered light was analyzed with a Spex Model 1400 double monochromator, a photomultiplier cooled to ~−25°, and a d.c. ammeter. Neon lines were used for calibration and the frequency accuracy was 1 cm^{-1} 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.[1a,6–8]

Similarly, BF_3 and ClO_2F 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^{-1}) for the heterogeneous equilibrium

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

is a straight line. The equation $\log P_{mm} = 11.1482 - (2623.1/T)$ represents these data in the temperature range −23 to 22°. The standard error of the estimate of log P was 0.003 which corresponds to 0.7% deviation in pressure. The index of correlation (ρ) 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_{mm} *vs.* T^{-1} curve, $\Delta H_d°$[9] = 24.01 kcal mol^{-1} was found. From $\Delta F°_T = -RT \ln Kp$(atm), a free energy change, $\Delta F°_{298} = 2.264$ kcal mol^{-1}, and from $\Delta S°_T = (\Delta H° - \Delta F°_T)T^{-1}$, an entropy change, $\Delta S°_{298} = 72.92$ cal deg^{-1} mol^{-1}, were found for the dissociation process at 25°. A heat of formation of $ClO_2^+BF_4^-(s)$, $\Delta H_f°_{298} = -303$ kcal mol^{-1}, was calculated based upon $\Delta H_f°_{298}$[ClO_2-

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[3] A. Engelbrecht, *Angew. Chem.*, **66**, 442 (1954).

[4] K. O. Christe and A. E. Pavlath, *Z. Anorg. Allgem. Chem.*, **335**, 210 (1965).

[5] E. K. Plyler, A. Danti, L. R. Blaine, and E. D. Tidwell, *J. Res. Natl. Bur. Std.*, **64**, 841 (1960).

[6] M. Schmeisser and F. L. Ebenhöch, *Angew. Chem.*, **66**, 230 (1954).

[7] M. Schmeisser and W. Fink, *ibid.*, **69**, 780 (1957).

[8] C. J. Schack and D. Pilipovich, paper presented at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968; see also C. J. Schack and D. Pilipovich, *Inorg. Chem.*, in press.

[9] It is not strictly correct to infer that the measured heat of reaction for the dissociation process equals the thermodynamic heat of dissociation. This would only be appropriate if the complex were in the gas phase or if the heat of sublimation of the complex were zero. However, for convenience, $\Delta H_d°$ will be used throughout the text to mean the heat of reaction of a complete dissociation process of the type: complex(s) = gas + gas.

$F(g)]^{10} = -7$ kcal mol^{-1} and $\Delta H_f{}^\circ{}_{298}[BF_3(g)]^{11} = -271.65$ kcal mol^{-1}. 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,[9] 24.01 kcal mol^{-1}, obtained for $ClO_2{}^+BF_4{}^-$ is very close to the value of 23.6 kcal mol^{-1} found[12] for the similar complex $ClF_2{}^+BF_4{}^-$. 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 $ClO_2{}^+AsF_6{}^-$. 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[14,15]), an average volume of 17 to 18 Å^3 can be expected for each fluorine or oxygen atom in $ClO_2{}^+AsF_6{}^-$. Thus, values of 17.8 and 17.0 Å^3 have been reported for $IF_6{}^+AsF_6{}^-$ [16] and $NF_4{}^+AsF_6{}^-$,[17,18] 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^3 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 $ClF_2{}^+AsF_6{}^-$ (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^3 was calculated. The crystal structure of $ClF_2{}^+AsF_6{}^-$ can be considered as a tetragonally distorted face-centered-cubic cell which is quite common for $R(MX_6)$-type compounds.[19] The fact that the observed powder patterns and calculated unit cell dimensions differ considerably for $ClF_2{}^+AsF_6{}^-$ and $ClO_2{}^+AsF_6{}^-$ 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 $ClO_2{}^+AsF_6{}^-$. No absorption bands were observed in the infrared spectrum below 400 cm^{-1}. The 1296- and 1044-cm^{-1} bands were recorded under high-resolution conditions for both the dry powder sample at ambient temperature and the low-temperature sample to measure the ^{35}Cl-^{37}Cl isotope splitting. Ten measurements were made for each band pair resulting in an average frequency-difference value of 13.80 ± 0.19 cm^{-1} for ν_3 (B_1) and of 5.40 ± 0.07 cm^{-1} for ν_1 (A_1). The uncertainty is mainly due to the difficulty in accurately locating the band center. The ν_2 (A_1) band pair could

TABLE I
X-RAY POWDER DATA FOR $ClO_2{}^+AsF_6{}^-$ AND $ClF_2{}^+AsF_6{}^-$

$ClO_2{}^+AsF_6{}^-$ d, Å Obsd	$ClO_2{}^+AsF_6{}^-$ d, Å Calcd	Intens	*hkl*	$ClF_2{}^+AsF_6{}^-$ d, Å Obsd	$ClF_2{}^+AsF_6{}^-$ d, Å Calcd	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	3.74	w	200
3.65	3.67	vs	220	3.72		m	
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	500 430	2.29	2.30	vw	311
2.05	2.04	s	510	2.102	2.107	vw	204
2.013	2.011	vw	004 501	2.070	2.075	w	320
				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					

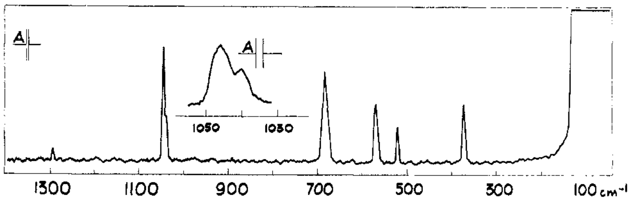

Figure 1.—Raman spectrum of solid $ClO_2{}^+AsF_6{}^-$. A indicates spectral slit width.

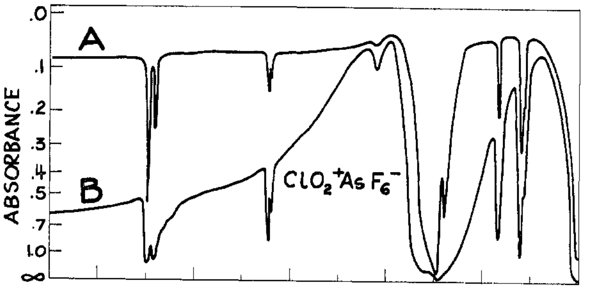

Figure 2.—Infrared spectrum of solid $ClO_2{}^+AsF_6{}^-$ as dry powder at ambient temperature (B) and as a film at low temperature (A).

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[10] J. Q. Weber of Rocketdyne estimated this value by comparison with bond energies of known Cl–O and Cl–F containing compounds.

[11] G. K. Johnson, H. M. Feder, and W. N. Hubbard, *J. Phys. Chem.*, **70**, 1 (1966).

[12] H. Selig and J. Shamir, *Inorg. Chem.*, **3**, 294 (1964).

[13] K. O. Christe and W. Sawodny, *ibid.*, **6**, 313 (1967).

[14] W. H. Zachariasen, *J. Am. Chem. Soc.*, **70**, 2147 (1948).

[15] F. H. Ellinger and W. H. Zachariasen, *J. Phys. Chem.*, **58**, 405 (1954).

[16] K. O. Christe and W. Sawodny, *Inorg. Chem.*, **6**, 1783 (1967).

[17] K. O. Christe, J. P. Guertin, and A. E. Pavlath, *Inorg. Nucl. Chem. Letters*, **2**, 83 (1966).

[18] R. A. Penneman, *Inorg. Chem.*, **6**, 431 (1967).

[19] R. W. G. Wyckoff, "Crystal Structures," Vol. III, Interscience Publishers, Inc., New York, N. Y., 1960, Chapter IX, p 5.

TABLE II

VIBRATIONAL SPECTRA OF $ClO_2^+AsF_6^-$ AND $ClO_2^+BF_4^-$ AND THEIR ASSIGNMENTS COMPARED WITH THOSE OF SO_2

Obsd freq, cm^{-1}				Assignment (point group)		
$ClO_2^+AsF_6^-$		$ClO_2^+BF_4^-$	SO_2[a]	XO_2 (C_{2v})	AsF_6^- (O_h)	BF_4^- (T_d)
Ir	R	Ir	Ir			
1296.4 m	1296.4 (1)	1308 m	1362 vs	ν_3 (B_1)		$\nu_1 + \nu_4$ (F_2)
1282 6 mw		1294 mw				
1043.7 mw	1044.4 (10)	1100–990 vs	1151 ms	ν_1 (A_1)		ν_3 (F_2)
1038.3 w	1039.1 (4)					
825 vw		772 mw			$\nu_2 + \nu_6$ ($F_{1u} + F_{2u}$)	
						ν_1 (A_1)
694 vs					ν_3 (F_{1u})	
680 m	684 (8)				ν_1 (A_{1g})	
569 mw	570 (5)				ν_2 (E_g)	
		532 w, sh				ν_4 (F_2) ^{10}B
		521 mw, sh				ν_4 (F_2) ^{11}B
521.0 m	521.3 (3)	518 m	518 m	ν_2 (A_1)		
517 sh					ν_4 (F_{1u})	
400 s						
	372 (5)				ν_5 (F_{2g})	

[a] See ref 18.

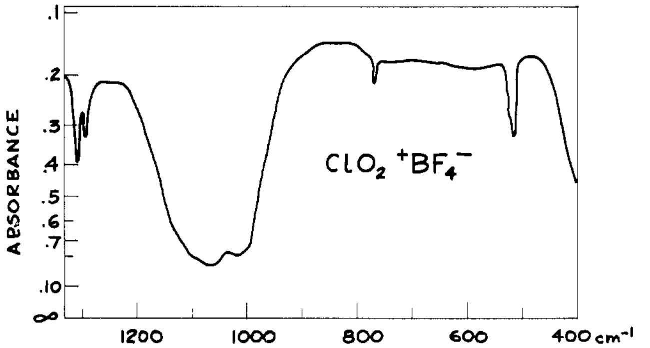

Figure 3.—Low-temperature infrared spectrum of solid ClO_2^+-BF_4^-.

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[20] for SO_2, 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 $ClF_2^+AsF_6^-$,[13] $NF_4^+AsF_6^-$,[23] $NF_2O^+AsF_6^-$,[24] and $IF_6^+AsF_6^-$.[16] The only deviations from the selection rules were observed for ν_2 (E_g) and ν_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.[13,16,23,24] It could be due to slight distortion of the AsF_6^- octahedron or crystal field effects.[13]

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

The three remaining band pairs observed in the spectra of both $ClO_2^+AsF_6^-$ and $ClO_2^+BF_4^-$ complexes should be due to ClO_2^+. A symmetric triatomic ion of the type XO_2^+, such as ClO_2^+, could be either linear or bent. Linear XO_2^+ has symmetry $D_{\infty h}$. The three normal modes of vibration are classified as $\Sigma_g^+ + \Pi_u + \Sigma_u^+$. Since linear XO_2^+ has a symmetry center, it follows the rule of mutual exclusion. Therefore, only Π_u and Σ_u^+ will be infrared active. Bent XO_2^+ has symmetry C_{2v}. The three normal modes of vibration

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[20] R. D. Shelton, A. H. Nielsen, and W. H. Fletcher, *J. Chem. Phys.*, **21**, 2178 (1953).

[21] K. O. Christe, unpublished results.

[22] D. A. Dows, *J. Chem. Phys.*, **31**, 1637 (1959).

[23] K. O. Christe, J. P. Guertin, A. E. Pavlath, and W. Sawodny, *Inorg Chem.*, **6**, 533 (1967).

[24] K. O. Christe and W. Maya, *ibid.*, **8**, 1253 (1969).

[25] J. Goubeau and W. Bues, *Z. Anorg. Allgem. Chem.*, **268**, 221 (1952).

[26] N. N. Greenwood, *J. Chem. Soc.*, 3811 (1959).

[27] J. A. A. Ketelaar and R. L. Fulton, *Z. Elektrochem.*, **64**, 641 (1960).

[28] K. O. Christe and W. Sawodny, *Inorg. Chem.*, **8**, 212 (1969).

are classified as 2 A_1 + B_1. All three modes will be infrared and Raman active. Furthermore, the frequency difference between ν_1 and ν_3 should be much larger for linear XY_2 than for bent XY_2. Since for ClO_2^+ three bands were observed in both the infrared and Raman spectra showing a frequency difference of only 250 cm^{-1} for the two stretching vibrations, the possibility of symmetry $D_{\infty h}$ is eliminated. This is not surprising since ClO_2^+ 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 ν_1 and ν_3 and since isoelectronic SO_2 is known to be a symmetric bent molecule and exhibits an infrared spectrum[20] very similar to that of ClO_2^+ (see Table II). However, slight distortion of bent ClO_2^+ (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_2. 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 ^{35}Cl and ^{37}Cl isotopes. The bands belonging to ^{37}Cl have the lower frequencies and lower relative intensities. The fact that ν_1 (A_1) shows a pronounced isotope splitting also eliminates a linear structure of symmetry $D_{\infty h}$.

The ClO_2^+ deformation vibration occurs in the same range as some of the ClF_x deformation vibrations. Furthermore, AsF_6^- and BF_4^- have a combination vibration, ($\nu_2 + \nu_3$) and ($\nu_1 + \nu_4$), respectively, at frequencies close to that of ν_3 (B_1) of ClO_2^+. Consequently, detection of small amounts of $ClO_2^+AsF_6^-$ or $ClO_2^+BF_4^-$ in the presence of $ClF_x^+AsF_6^-$ or ClF_x^+-BF_4^-, respectively, is difficult. Thus, some of the low-temperature infrared spectra reported previously[13,28] may have contained small amounts of ClO_2^+ containing salts. Distinction between ν_3 (B_1) of ClO_2^+ and (ν_2 + ν_3) of 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}Cl–^{37}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_2^+. However, the geometry of ClO_2^+ 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.[29] For ClO_2^+ 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

$$\cos\alpha = 1 - \frac{\nu'^2_3 - \nu_3^2}{m_0\left(\dfrac{\nu'^2_3}{m_{Cl}} - \dfrac{\nu_3^2}{m'_{Cl}}\right)}$$

Based on this relationship and the observed frequencies, an O–Cl–O bond angle of 114.0° is calculated for ClO_2^+. However, this value appears low since bond angles of 110.5 and 117.6° were reported[30] for ClO_2^- and ClO_2, respectively. For ClO_2^+ a further angle increase is likely and a value of 120° can be expected by analogy with the value of 119° reported[30] for isoelectronic SO_2. However, an increase of $\Delta\nu_3$ by 0.5 cm^{-1} would result in an angle of 120°. Such a small change in $\Delta\nu_3$ 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_1 vibration, two separate sets of F_{33} were calculated using the $^{35}ClO_2^+$ and $^{37}ClO_2^+$ frequencies, respectively. Table III shows the arithmetic mean of the two sets with a variance of ±0.01 mdyn/Å covering both the $^{35}ClO_2^+$ and $^{37}ClO_2^+$ values for all angles. For species A_1 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_1 force field, only the intersection point of the F_{11}/F_{12} ellipses for $^{35}ClO_2^+$ and $^{37}ClO_2^+$ was used since $\Delta\nu_2$ is not known with sufficient accuracy.

Table III shows that the valence force constant, f_r, and the deformation constant, f_α, exhibit only a slight bond angle dependence and have values of 8.96 ± 0.06 and 0.82 ± 0.03 mdyn/Å, respectively, for the angle range 115–125°. However, the two interaction constants f_{rr} and $f_{r\alpha}$ depend strongly on the bond angle and, hence, cannot be determined exactly. For the bond angle range 115–125°, f_{rr} and $f_{r\alpha}$ have values of -0.45 ± 0.13 and 0.24 ± 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[30] using an approximating method[31] which for the related ClO_2 radical resulted in values[32] very close to those[33] of a

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(29) (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_2 and SeO_2 from isotopic frequencies.

(30) H. Siebert, "Anwendungen der Schwingungsspektroskopie in der Anorganischen Chemie," Springer-Verlag, Berlin, 1966.

(31) W. Sawodny, A. Fadini, and K. Ballein, *Spectrochim. Acta*, **21**, 995 (1965).

(32) J. Goubeau, *Angew. Chem. Intern. Ed. Engl.*, **5**, 567 (1966).

(33) 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, deg	Symmetry force constants				Internal force constants	
	$F_{11} = f_r + f_{rr}$	$F_{12} = \sqrt{2}f_{r\alpha}$	$F_{22} = f_\alpha$	$F_{33} = f_r - f_{rr}$	f_r	f_{rr}
105	8.27 ± 0.03	0.97 ± 0.03	0.94 ± 0.01	10.04 ± 0.01	9.16 ± 0.01	−0.89 ± 0.02
110	8.36 ± 0.02	0.75 ± 0.02	0.89 ± 0	9.81 ± 0	9.09 ± 0.01	−0.73 ± 0.01
115	8.44 ± 0.02	0.54 ± 0.01	0.85 ± 0	9.60 ± 0.01	9.02 ± 0.01	−0.58 ± 0.02
120	8.51 ± 0.02	0.35 ± 0.01	0.82 ± 0	9.40 ± 0.01	8.96 ± 0.01	−0.45 ± 0.02
125	8.57 ± 0.01	0.16 ± 0.01	0.80 ± 0	9.22 ± 0.01	8.90 ± 0	−0.33 ± 0.01

GVFF. The data listed for ClO_2 and SO_2 are GVFF values computed with the aid of centrifugal distortion constants,[33,34] which for SO_2 are almost identical with the GVFF values computed from isotopic shifts.[35] 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[36] and an increasing s character of the chlorine orbitals involved in the σ bonds, changing from mainly sp^3 in ClO_2^- to sp^2 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_4–NF_4^+ [23] and OCl_2–FCl_2^+,[28] and have been attributed[23,28] to increasing bond polarity. It is difficult to rationalize the relatively high negative value of f_{rr} for ClO_2^+. However, similar negative values were found for f_{rr} of ClO_2F[37] and ClO_3F.[31]

TABLE IV

INTERNAL FORCE CONSTANTS OF ClO_2^-, ClO_2, ClO_2^+, AND SO_2 (MDYN/Å)

	f_r	f_{rr}	$f_{r\alpha}$	f_α
ClO_2^- [a]	4.26	0.11	0.02	0.52
ClO_2 [b]	7.02	−0.17	0.01	0.65
ClO_2^+	8.96 ± 0.06	−0.45 ± 0.13	0.24 ± 0.13	0.82 ± 0.03
SO_2 [c]	10.01	0.02	0.19	0.79

[a] See ref 30. [b] See ref 33. [c] See ref 34.

It should be interesting to compare ClO_2^+ with ClO_2F. Smith, Begun, and Fletcher have reported[37] a modified valence force field for ClO_2F 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_2 part in $O_2Cl^{\delta+}$–$F^{\delta-}$ should be very similar to ClO_2^+. Indeed the agreement between the values found for ClO_2^+ and those reported for ClO_2F (f_r = 9.07, f_{rr} = −0.12, $f_{r\alpha}$ = 0.38, and f_α = 1.06 mdyn/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.

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(34) D. Kivelson, *J. Chem. Phys.*, **22**, 904 (1954).

(35) S. R. Polo and M. K. Wilson, *ibid.*, **22**, 900 (1954).

(36) J. Goubeau, *Angew. Chem.*, **69**, 77 (1957).

(37) D. F. Smith, G. M. Begun, and W. H. Fletcher, *Spectrochim. Acta*, **20**, 1763 (1964).