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Reactions of Ozone with Covalent Hypohalites

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The reactions of pure ozone with a series of covalent hypohalites were examined. With $ClOClO_3$, $ClOSO_2F$, $BrONO_2$, and $BrOClO_3$ oxidative oxygenations of the terminal halogen occurred giving respectively $O_2ClOClO_3$, O_2ClOSO_2F, O_2BrONO_2, and the new compound $O_2BrOClO_3$. Similar conditions with $ClONO_2$ produced exclusively $NO_2^+ClO_4^-$, constituting a new synthesis of this powerful oxidizer. With $ClOCF_3$ and $BrOSO_2F$ no oxidation was noted. For comparison, chlorine dioxide was also oxidized to chlorine hexoxide using the same experimental conditions. The nature of the products prepared by different methods and all having the empirical composition Cl_2O_6 was investigated by mass and infrared matrix-isolation spectroscopy. It is concluded that above its melting point "Cl_2O_6" has the oxygen-bridged chloryl perchlorate structure $O_2ClOClO_3$. The infrared spectrum of matrix-isolated ClO_2 was also recorded and its $^{35}Cl-^{37}Cl$ isotopic shifts were measured.

Introduction

Covalent hypohalite compounds are highly reactive and synthetically useful reagents.[1] However, nearly all of the known chemistry of these materials centers on their reactions involving cleavage of the halogen-oxygen bond. For example, $BrOSO_2F$ was used[2] to replace the chlorines in CCl_4 giving $C(OSO_2F)_4$, while $ClOSO_2F$ was employed[3] to produce $ClOClO_3$ from $CsClO_4$. In other cases, $ClOSO_2F$[4] and $ClOClO_3$[5] were shown to add across olefinic double bonds forming $Cl\text{-}\overset{|}{\underset{|}{C}}\text{-}\overset{|}{\underset{|}{C}}OSO_2F$ and $Cl\text{-}\overset{|}{\underset{|}{C}}\text{-}\overset{|}{\underset{|}{C}}\text{-}OClO_3$ derivatives. It appeared interesting to synthesize the corresponding halites, halates, or perhalates by oxidative oxygenation of the terminal halogen. The only report of such an oxidation was given by Schmeisser and Taglinger[6] on the ozonization of $BrONO_2$ at −78° according to

$$BrONO_2 + 2O_3 \rightarrow O_2BrONO_2 + 2O_2$$

This successful synthesis of bromyl nitrate suggested the possibility of carrying out similar reactions of O_3 with other XO species. Accordingly, we examined the reactions of ozone with $ClOClO_3$, $ClOSO_2F$, $ClONO_2$, $ClOCF_3$, $BrOClO_3$, and $BrOSO_2F$. For comparison, the known[6,7] oxidative ozonizations of $BrONO_2$ and ClO_2 were carried out under our reaction conditions.

Experimental Section

Apparatus and Materials. The equipment used in this work has previously been described.[8] Mass spectra were recorded on a Quad 300 (Electronic Associates, Inc.) quadrupole mass spectrometer using a passivated all stainless steel inlet system. Infrared spectra were recorded on a Perkin-Elmer Model 457 spectrometer using the previously described matrix-isolation technique.[9] Literature methods were used to synthesize $ClOClO_3$,[3] $ClOSO_2F$,[8] $ClONO_2$,[10] $ClOCF_3$,[11] ClO_2,[12] $BrOClO_3$,[13] and $BrONO_2$.[6] Since hypobromites cannot be transferred without decomposition, they were synthesized directly in the ozonization vessel from Br_2 or BrCl and a slight excess of the corresponding hypochlorites. The undesired by-products and impurities were removed prior to addition of solvent and ozone.

Ozone was prepared by glow discharge of O_2 (Matheson Co.) in a Pyrex U tube cooled with liquid nitrogen. A 15-kV power supply provided the discharge through internal copper electrodes and the conversion of O_2 to O_3 was followed manometrically. After volumetric measurement, the O_3 was immediately loaded into a precooled reactor. Approximately 1 mmol of O_3 was obtained from each batch. Larger quantities could be easily prepared but were avoided for safety considerations.

General Method. Essentially the same technique was applied in all the reactions. The freshly prepared, purified, and measured hypohalite was placed in the reactor at −196°. Solvent CF_3Cl or $CFCl_3$, when used, was added, followed by a measured amount of O_3 both being condensed into the reactor cooled to −196°. The closed reactor was maintained at the desired reaction temperature in a freezer for a specified period. Subsequently, the reactor was recooled to −196° and the by-product O_2 pumped away and measured. Solvent, unreacted starting material, and products were separated by fractional condensation in a series of U traps cooled to appropriate temperatures. Product identification was based on combinations of infrared and mass spectroscopy, vapor pressure measurements, and elemental analyses.

Discussion

Caution! Most of the hypohalites employed in this study are potential explosives. Also, the use of pure ozone can be hazardous and two explosions were encountered with it. Safety precautions must be adhered to when working with these materials and the reactions should be limited a millimole scale.

The results of representative reactions are summarized in Table I. The nature of the reactor (*i.e.*, 304 or 316 stainless steel cylinders and FEP Teflon or sapphire tubes all equipped with stainless steel valves) did not appear to influence the course of the reactions.

The $ClOClO_3$-O_3 System. For chlorine perchlorate it was found that oxidation occurred under a variety of conditions according to the equation

$$ClOClO_3 + 2O_3 \rightarrow O_2ClOClO_3 + 2O_2$$

A virtually quantitative conversion of $ClOClO_3$ to Cl_2O_6 was achieved as was also established by a very good oxygen material balance. When short reaction times were used, most of the unreacted O_3 could be recovered undecomposed. This indicates that each O_3 molecule contributed only one oxygen atom to converting Cl_2O_4 to Cl_2O_6. Large excess of O_3 did not cause any further oxidation of $O_2ClOClO_3$. Thus, O_3-$ClOClO_3$ (Cl_2O_7) was never observed in these systems.

Properties and Structure of Cl_2O_6. The exact nature of "Cl_2O_6" has as yet not been established. The two most

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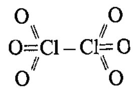
(1) K. Dehnicke, *Chimia*, 27, 309 (1973).
(2) D. D. DesMarteau, *Inorg. Chem.*, 7, 434 (1968).
(3) C. J. Schack and D. Pilipovich, *Inorg. Chem.*, 9, 1387 (1970).
(4) W. P. Gilbreath and G. H. Cady, *Inorg. Chem.*, 2, 496 (1963).
(5) C. J. Schack, D. Pilipovich, and J. F. Hon, *Inorg. Chem.*, 12, 897 (1973).
(6) M. Schmeisser and L. Taglinger, *Chem. Ber.*, 94, 1533 (1961).
(7) H. J. Schumacher and G. Stieger, *Z. Anorg. Allg. Chem.*, 184, 272 (1929).
(8) C. J. Schack and R. D. Wilson, *Inorg. Chem.*, 9, 311 (1970).
(9) K. O. Christe and D. Pilipovich, *J. Amer. Chem. Soc.*, 93, 51 (1971).
(10) C. J. Schack, *Inorg. Chem.*, 6, 1938 (1967).
(11) C. J. Schack and W. Maya, *J. Amer. Chem. Soc.*, 91, 2902 (1969).
(12) W. S. Hutchinson and R. J. Derby, *Ind. Eng. Chem.*, 37, 813 (1945).
(13) C. J. Schack, K. O. Christe, and R. D. Wilson, *Inorg. Chem.*, 10, 1078 (1971).

Table I. Ozone Reactions

Hypohalite (mmol)	Amt of O_3, mmol	Solvent	Temp, °C	Time, hr	Products[a] (mmol)
$ClOClO_3$ (1.30)	2.86	None	−78	24	Cl_2O_6 (0.47), $ClOClO_3$ (0.83)
$ClOClO_3$ (1.35)	3.24	CF_3Cl or none	−45	40	Cl_2O_6 (1.35)
ClO_2 (1.23)	3.16	None	−45	18	Cl_2O_6 (0.61)
$ClOSO_2F$ (1.06)	2.30	None	−45	70	ClO_2SO_3F (1.03)
$ClONO_2$ (0.73)	2.55	None	−45	66	NO_2ClO_4 (0.39), $ClONO_2$ (0.33)
$ClONO_2$ (1.08)	3.24	CF_3Cl	−45	42	NO_2ClO_4 (0.74), $ClONO_2$ (0.34)
$ClONO_2$ (1.03)	4.04	CF_3Cl	−45	72	NO_2ClO_4 (0.92), Cl_2
$ClOCF_3$ (1.02)	2.60	None	−45	300	$ClOCF_3$ (0.98), COF_2
$BrOClO_3$ (1.59)	2.98	None	−45	72	$Br_2 + Cl_2 + BrCl$ (1.58), O_2 (7.41)
$BrOClO_3$ (1.29)	3.06	CF_3Cl	−45	72	BrO_2ClO_4 (1.28)
$BrONO_2$ (1.06)	2.80	$CFCl_3$	−45	72	BrO_2NO_2 (1.01)
$BrONO_2$ (1.00)	3.15	$CFCl_3$	−23	100	O_2 (5.42), Br_2, NO_2
$BrOSO_2F$ (1.25)	3.37	None	−45	130	O_2 (5.14), $BrOSO_2F$ (1.20), Br_2, $S_2O_5F_2$

[a] Except where noted, by-product O_2 was always found in ratios expected for nO_3 + substrate → nO_2 + substrate·O_n in addition to small amounts of O_2 resulting from the decomposition of O_3.

likely structures are the symmetric Cl-Cl-bridged model I and the asymmetric oxygen-bridge model II.[14] Another structure suggested[15] as very probable is the double-oxygen-bridged model III. However, several severe shortcomings make this model unlikely. In both versions, IIIA and IIIB, at least one Cl must assume an energetically unfavorable pentacoordination.[16] In addition, IIIA would be a diradical which disagrees with the diamagnetism observed[17] for pure Cl_2O_6.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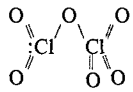
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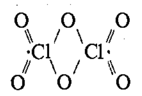
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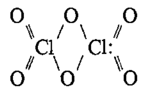
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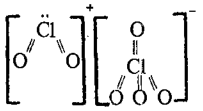
IV

Most frequently, Cl_2O_6 is considered[14,15] to possess structure I based on early work[18] which reported the detection of considerable paramagnetism in the liquid and solid phases. This paramagnetism was attributed to the ClO_3 radical being in equilibrium with the Cl_2O_6 dimer according to $Cl_2O_6 \rightleftarrows 2ClO_3$. The surprisingly low value of 1.5 kcal/mol for the "dissociation energy" of this supposed quilibrium was generally interpreted as an indication for Cl_2O_6 having structure I with an extremely weak Cl-Cl bond. However, more recently it was shown[17] that the paramagnetic species present in small concentrations in condensed Cl_2O_6 is ClO_2 and that the uv-visible spectrum attributed to gaseous ClO_3 closely resembles that of ClO.[15] Chlorine trioxide radicals are very difficult to obtain and were found in Cl_2O_6 only under extreme conditions, *i.e.*, at −196° after irradiation by ^{60}Co γ irradiation.[17] Additional doubts about the validity of model I stem from its reaction chemistry[14] and the vibrational spectrum of the solid[19] which suggest the ionic structure ClO_2^+-ClO_4^- (model IV). In view of the different known synthetic methods[3,7,14] for preparing a product of the composition Cl_2O_6 and of the known existence of two forms of $(ClO_2)_n$, *i.e.*, ClO_2[14] and oxygen bridged Cl_2O_4,[3] it appeared desirable to establish the identity of the various Cl_2O_6 compositions and, if possible, to determine the structure of the isolated free species. For this purpose we have studied samples of Cl_2O_6 prepared by three different synthetic methods (eq 1-3).

$$2ClO_2 + 2O_3 \rightarrow Cl_2O_6 + 2O_2 \quad \text{(ref 7)} \qquad (1)$$

$$ClOClO_3 + 2O_3 \rightarrow Cl_2O_6 + 2O_2 \quad \text{(this work)} \qquad (2)$$

$$ClOClO_3 \rightarrow Cl_2O_6 \quad \text{(ref 3)} \qquad (3)$$

The identical nature of the different Cl_2O_6 samples was established by their elemental analyses after decomposition at elevated temperature, their physical appearance, and properties. They were orange solids melting near 0° to form dark red liquids. They exhibited only several millimeters vapor pressure near ambient temperature. On standing at 22°, slow gas evolution was noted and the gas pressure increased gradually. This was found to be caused by the decomposition of Cl_2O_6 resulting in the formation of ClO_2, Cl_2, and O_2.

Spectroscopic Studies. Additional support for the various Cl_2O_6 compositions being identical was obtained by mass and infrared matrix-isolation spectroscopy. Previous reports on the mass spectrum[20,21] of Cl_2O_6 show some discrepancy. Cordes and Smith[20] observed a weak ClO_3^+ ion as the highest *m/e* from Cl_2O_6. However, Fisher[21] found no ClO_x^+ ions above ClO_2^+, but his samples showed appreciable amounts of $HClO_4$ as impurity. In this work, samples without $HClO_4$ gave a small (5% of base) peak for ClO_3^+. Even samples with $HClO_4$ exhibited a modest but reproducible ClO_3^+ peak after the spectrum was corrected for that impurity.

For the infrared study, Cl_2O_6 samples were isolated in an N_2 matrix (MR 1:1000) at 4°K. All three samples exhibited the same characteristics. Unfortunately, the spectra were rather complex. In agreement with the previous esr study,[17] it was found that the gas phase above liquid Cl_2O_6 consisted mainly of ClO_2. The infrared spectrum of matrix-isolated ClO_2 closely corresponded to the well-known gas-phase spectrum.[22] The ^{35}Cl-^{37}Cl isotopic shifts were measured for the matrix-isolated species. They are compared in Table II with the previous measurements[22-24] which showed considerable discrepancy.

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[14] M. Schmeisser and K. Brandle, *Advan. Inorg. Chem. Radiochem.*, 5, 58 (1963).

[15] A. J. Downs and C. J. Adams in "Comprehensive Inorganic Chemistry," Vol. 2, Bailar, Emeleus, Nyholm, and Trotman-Dickenson, Ed., Pergamon Press, Oxford, 1973, pp 1372-1374.

[16] K. O. Christe, *Pure Appl. Chem.*, in press.

[17] V. N. Belevskii and L. T. Bugaenko, *Russ. J. Inorg. Chem.*, 12, 1203 (1967).

[18] J. Farguharson, C. F. Goodeve, and F. D. Richarson, *Trans. Faraday Soc.*, 32, 790 (1936).

[19] A. C. Pavia, J. Pascal, and A. Potier, *C. R. Acad. Sci.*, 272, 1495 (1971).

[20] H. F. Cordes and S. R. Smith, *J. Chem. Eng. Data*, 15, 158 (1970).

[21] I. P. Fisher, *Trans. Faraday Soc.*, 64, 1852 (1968).

[22] A. H. Nielsen and P. J. H. Woltz, *J. Chem. Phys.*, 20, 1878 (1952).

[23] J. K. Ward, *Phys. Rev.*, 96, 845 (1954).

[24] A. W. Richardson, R. W. Redding, and J. C. D. Brand, *J. Mol. Spectrosc.*, 29, 93 (1969).

Table II. ^{35}Cl–^{37}Cl Isotopic Shifts (cm^{-1}) of ClO_2

	^{35}Cl freq	Isotopic shifts				
					Ref 24	
	This study	This study	Ref 22	Ref 23	Ir	Uv
ν_1	950	5.8 ± 0.2		6.41	4.8	5.7
ν_2	452	2.9				3.3
ν_3	1104	11.4	11.5		12.7	

No evidence could be found in our spectra for bands showing the frequencies and intensities expected for a free ClO_3 radical. This result agrees with the previous esr study[17] and indicates either that Cl_2O_6 does not appreciably dissociate into ClO_3 or that the ClO_3 radical is highly unstable and rapidly decomposes into ClO_2 and oxygen. The first alternative is more in agreement with our expectations for a structure containing a strongly polarized oxygen bridge (see below). Thus, the O_2Cl–O bond should be considerably weaker than the O–ClO_3 bond and, therefore, the former should preferentially break. This should result in the formation of ClO_2 and (unstable) ClO_4 instead of ClO_3 radicals.

In addition to ClO_2, the matrix-isolation spectra always exhibited bands due to $HOClO_3$.[25] To positively identify the bands due to $HOClO_3$ in an N_2 matrix, we have prepared a sample of pure $HOClO_3$ and recorded its spectrum. In addition to bands attributable to the monomer, features due to associated $HOClO_3$ were observed. The intensity of the latter was a function of the dilution ratio.

To suppress the bands due to ClO_2 and $HOClO_3$, N_2 was rapidly swept over liquid Cl_2O_6 and immediately frozen out on the cold CsI window of the ir cell. Under these conditions, at least two novel species were observed in addition to ClO_2 and $HOClO_3$. These two species, designated A and B, showed the following principal absorptions (cm^{-1}): A, 1275 (vs), 1043 (s), 1041 (m), 1008 (w), 950, 702 (vs), 658 (w), 648 (w), 620 (w), 585 (s), 512 (w); B, 1240 (s), 1028 (vs), 624 (vs), 484 (vs), 374 (vs). These bands exhibit frequencies and to some extent ^{37}Cl isotopic splittings in agreement with those expected for covalent chlorato or perchlorato compounds. In particular, species A shows a very intense band in the frequency region expected[26] for an antisymmetric stretch of a Cl–O–Cl bridge in addition to bands occurring in the ClO_3 and ClO_2 stretching modes region.[26] Therefore, this set of bands might be due to a Cl–O–Cl-bridged Cl_2O_6 species, such as model II. [The set of bands ascribed to species B somewhat resembles that of $FClO_2$[27] shifted to a lower frequency. This indicates an $XClO_2$ type species with X being less electronegative than F. Possibly, this species could be $HOClO_2$ which might be expected from the hydrolysis of $O_2ClOClO_3$ according to $O_2ClOClO_3 + H_2O \rightarrow HOClO_3 + HOClO_2$.] However, unambiguous identification and assignment of the bands are not possible owing to the size and low symmetry of these species and to the complexity of the rest of the spectrum.

In summary, our spectroscopic studies indicate that the three "Cl_2O_6" species obtained by the three different synthetic methods are indeed identical. Furthermore, the low-temperature, high-yield oxidation of the Cl–O–Cl-bridged starting material $ClOClO_3$ combined with the results from the other more recent studies[14,15,17,19] show that Cl_2O_6 has the oxygen-bridged structure II and not the Cl–Cl-bridged structure I. Therefore, the assumption of a previously postulated[14] rearrangement of Cl_2O_6 from model I to model II used to reconcile its reaction chemistry with a basic Cl–Cl-bridged structure is unwarranted. On the other hand, for the oxygen-bridged structure II transformation into the ionic structure IV should be very facile requiring no significant rearrangements. The low volatility of Cl_2O_6, its high melting point, and its readiness to change to an ionic structure in the solid also indicate for the liquid a strong polarization of the Cl–O–Cl bridge in the direction toward $O_2Cl^+OClO_3^-$. This structural behavior of Cl_2O_6 closely resembles that of N_2O_5 which in the free state has a covalent oxygen-bridged structure but in the solid state has the ionic structure $NO_2^+NO_3^-$.[28]

The $BrOClO_3$–O_3 System. The novel process for oxygenation of the terminal chlorine of $ClOClO_3$ was applied to $BrOClO_3$. Surprisingly, it was found that neat O_3 and $BrOClO_3$ in the temperature range of −78 to −45° reacted to cause their complete degradation to the elements. An effort was therefore made to moderate the reaction through the use of CF_3Cl as a solvent. This was successful and the reaction observed at −45° was

$$BrOClO_3 + 2O_3 \rightarrow O_2BrOClO_3 + 2O_2$$

This stoichiometry was confirmed by an excellent oxygen material balance and by elemental analysis of the product which showed six oxygen atoms were present for each BrCl. The novel compound $O_2BrOClO_3$ is a bright orange solid that does not melt below −35°. Since decomposition begins at higher temperatures and owing to its nonvolatility, we were unable to determine reliably other properties. Additional proof for its composition was obtained by a displacement reaction with FNO_2 carried out at −45°. The following reaction was observed

$$O_2BrOClO_3 + FNO_2 \rightarrow NO_2ClO_4 + [FBrO_2]$$

The displacement was slow, requiring several days. While the solid nitronium perchlorate was found in quantitative yield (1.35 mmol of NO_2ClO_4 from 1.35 mmol of $O_2BrOClO_3$), the $FBrO_2$ decomposed to the elements.

The $ClOSO_2F$–O_3 and $BrOSO_2F$–O_3 Systems. The reaction of chlorine fluorosulfate and ozone was examined in view of the above results and the fact that the predicted product (O_2ClOSO_2F) is well known from other routes.[14,29] The following reaction was observed

$$ClOSO_2F + 2O_3 \rightarrow O_2ClOSO_2F + 2O_2$$

Yields above 90% were readily realized at temperatures up to 0°. The use of a solvent was not required and was not investigated. With a large excess of O_3 additional oxygen uptake was not observed.

Bromine fluorosulfate and ozone reacted only incompletely. The main reaction was decomposition of O_3 to O_2 accompanied by some degradation of the $BrOSO_2F$. No evidence for O_2BrOSO_2F was obtained.

The $ClONO_2$–O_3 System. Ozone and chlorine nitrate did not react at −78° in the absence of a solvent. However, when a solvent was used or the temperature was raised to −45°, chlorine was surprisingly oxidized to the +VII oxidation state as shown

$$ClONO_2 + 3O_3 \rightarrow NO_2^+ClO_4^- + 3O_2$$

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(25) P. A. Giguere and R. Savoie, *Can. J. Chem.*, 40, 495 (1962).

(26) K. O. Christe, C. J. Schack, and E. C. Curtis, *Inorg. Chem.*, 10, 1589 (1971).

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

(28) R. Teranishi and J. C. Decius, *J. Chem. Phys.*, 22, 896 (1954).

(29) H. A. Carter, A. M. Qureshi, and F. Aubke, *Chem. Commun.*, 1461 (1968).

Thus, the covalent hypochlorite group was oxidized to the perchlorate anion. An excellent material balance was obtained for this reaction. Again only one oxygen from each ozone was added to the substrate. Furthermore, it was found that with a deficiency of O_3 or with short reaction periods, the only products were nitronium perchlorate and unreacted chlorine nitrate. Other intermediate oxidation products were not observed and, hence, must have been more reactive than $ClONO_2$. The white solid was readily identified as $NO_2^+ClO_4^-$ by its infrared spectrum[30] and comparison to an authentic sample. This reaction represents a new process for preparing nitronium perchlorate. Its main advantage consists of the elimination of ClO_2, one of the two shock-sensitive materials required for the conventional[31] $NO_2^+ClO_4^-$ synthesis.

The $BrONO_2$-O_3 System. The $BrONO_2$-O_3 reaction has previously been reported[6] to yield O_2BrONO_2. We reinvestigated this system since it now appeared to be a promising synthetic route to the novel and interesting compound $NO_2^+BrO_4^-$. All effort to this end, however, failed since at or below −45°, the only product was O_2BrONO_2, while at higher temperatures, degradation of the bromyl intermediate was encountered.

The CF_3OCl-O_3 System. Prolonged contact of trifluoromethyl hypochlorite with neat ozone at −45° did not result in any oxygenation of the chlorine or other reaction. Thus, CF_3OClO_3, a compound recently obtained by another synthetic approach,[32] was not observed.

General Aspects. Comparison of the results of the present study raises an interesting question. Whereas covalent hypochlorite groups are generally oxidized by O_3 to the O_2ClO group, *i.e.*, to chlorine (+V), the chlorine in $ClONO_2$ is oxidized to the +VII state. This is surprising since $ClOClO_3$ and $ClONO_2$ are both covalent hypochlorites of similar structure and reactivity, and the perchlorato and nitrato group are of similar electronegativity. Comparison of the resulting ozonization products, however, reveals a marked difference. The products, in which the original hypochlorite chlorine is oxidized to the +V oxidation state, are mainly covalent and polarized toward the $ClO_2^+X^-$ type structure where X^- can be, for example, ClO_4^- or SO_3F^-. In the case of $ClONO_2$, however, the hypochlorite chlorine ends up in the anion of the product $NO_2^+ClO_4^-$. Since cations are more difficult to oxidize and are stronger oxidizers than anions of the same oxidation state,[16] oxidation of $ClONO_2$ to $NO_2^+ClO_4^-$ is still possible, while formation of a covalent O_3ClO group or of the hypothetical ClO_3^+ cation is not. The ease of NO_2^+ formation is due to the fact that XNO_2 type compounds, such as FNO_2, are strong Lewis bases, whereas $XClO_2$ type compounds are amphoteric.[14,33]

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Registry No. O_3, 10028-15-6; $ClOClO_3$, 27218-16-2; $O_2ClOClO_3$, 52225-66-8; $BrOClO_3$, 32707-10-1; $O_2BrOClO_3$, 52225-67-9; $ClOSO_2F$, 13997-90-5; O_2ClOSO_2F, 24114-30-5; $ClONO_2$, 14545-72-3; $NO_2^+ClO_4^-$, 17495-81-7; ClO_2, 10049-04-4.

[30] J. W. Nebgen, A. D. McElroy, and H. F. Klodowski, *Inorg. Chem.*, 4, 1796 (1965).

[31] E. W. Lawless and I. C. Smith, "Inorganic High-Energy Oxidizers," Marcel Dekker, New York, N. Y., 1968, p 176.

[32] C. J. Schack, D. Pilipovich, and K. O. Christe, *Inorg. Nucl. Chem. Lett.*, 10, 449 (1974).

[33] K. O. Christe, C. J. Schack, D. Pilipovich, and W. Sawodny, *Inorg. Chem.*, 8, 2489 (1969).

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Metal Complexes as Ligands. V.[1] The Crystal and Molecular Structures of Tris(bis(triphenylphosphine)silver(I)) Tris(dithiooxalato)iron(III) and -aluminum(III), $[Ag(P(C_6H_5)_3)_2]_3M(O_2C_2S_2)_3$, M = Fe(III) and Al(III)

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Tris(bis(triphenylphosphine)silver(I)) tris(dithiooxalato)iron(III), A, crystallizes in the trigonal space group $P\bar{3}$ with two molecules per unit cell. The cell dimensions are $a = 19.984$ (6) Å and $c = 15.302$ (11) Å. The cell dimensions of the corresponding, isomorphous, aluminum(III) complex (B) are $a = 19.896$ (5) Å and $c = 15.251$ (6) Å. Intensity data for both A and B were collected with a four-circle computer-controlled diffractometer using the θ–2θ scan technique. In both A and B the carbon atoms in the phenyl rings were constrained to refine as groups of fixed geometry, and all the remaining atoms were refined with anisotropic thermal parameters. Refinement by full matrix least squares of 157 parameters on 2533 data for A and 157 parameters on 1862 data for B gave final R values of 0.051 for A and 0.052 for B. The central metal atom is octahedrally coordinated by the O,O "bites" of three dithiooxalate ligands, and the $Ag(PPh_3)_2^+$ cations interact at the S,S "bite" of each ligand. Average values of selected structural parameters involving the silver and the central metal atom are as follows: For A: Fe–O, 2.003 (6) Å; Ag–S, 2.59 (1) Å; Ag–P, 2.47 (1) Å; ϕ (trigonal twist angle), 36.9°; O–Fe–O (intraligand), 77.8 (2)°; S–Ag–S, 83.3 (1)°; P–Ag–P, 115.2 (1)°. For B: Al–O, 1.889 (8) Å; Ag–S, 2.59 (1) Å; Ag–P, 2.48 (1) Å; ϕ, 47.0°; O–Al–O (intraligand), 82.5 (4)°; S–Ag–S, 83.2 (1)°; P–Ag–P, 113.4 (2)°.

Introduction

In the dithiooxalate dianion ($S_2C_2O_2^{2-}$) (Figure 1), the presence of four donor atoms and the possibilities of charge delocalization on either the O,O or the S,S "bite" results in a versatile ligand with unique coordination properties.[3] The

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[1] Part IV: D. Coucouvanis, N. C. Baenziger, and S. M. Johnson, *Inorg. Chem.*, 13, 1191 (1974).

[2] Alfred P. Sloan Fellow, 1972–1974.

[3] (a) D. Coucouvanis, N. C. Baenziger, and S. M. Johnson, *J. Amer. Chem. Soc.*, 95, 3875 (1973); (b) D. Coucouvanis, and D. Piltingsrud, *ibid.*, 95, 5556 (1973), and references therein.