Gas-Phase Structures of Chlorine Nitrate and Bromine Nitrate (ClONO₂ and BrONO₂)

Bernd Casper,[†] Peter Lambotte,[‡] Rolf Minkwitz,[‡] and Heinz Oberhammer^{*,†}

Institut für Physikalische und Theoretische Chemie, Universität Tübingen, D-7400 Tübingen, Germany, and Institut für Anorganische Chemie, Universität Dortmund, D-4600 Dortmund, Germany

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The gas-phase structure of chlorine nitrate was determined by joint analysis of electron diffraction intensities and rotational constants. The structure of bromine nitrate was derived from electron diffraction data alone. Both nitrates have planar structures, and the following geometric parameters were obtained (r_a distances in angstroms and \angle_{α} angles in degrees; error limits are 2σ values and include a possible scale error of 0.1% for BrONO₂): for ClONO₂, $r_a(N=O) = 1.196(1)$, $r_a(N=O) = 1.499(3)$, $r_a(O=Cl) = 1.673(2)$, $\angle_{\alpha}(O=N=O) =$ 132.6(5), $\angle_{\alpha}(O-N=O_c) = 118.6(3)$, $\angle_{\alpha}(O-N=O_t) = 108.8(3)$, $\angle_{\alpha}(N-O-Cl) = 113.0(3)$; for BrONO₂, r_a -(N=O) = 1.205(3), $r_a(N=O) = 1.456(5)$, $r_a(O=Br) = 1.829(4)$, $\angle_{\alpha}(O=N=O) = 133.9(8)$, (O-N=O_c) = 119.5(6), $\angle_{\alpha}(O-N=O_t) = 106.6(5)$, $\angle_{\alpha}(N=O-Br) = 113.9(8)$. The gas-phase structure for ClONO₂ is compared to the crystal structure and to ab initio predictions. The results for both compounds are discussed together with those of other covalent nitrates XONO₂ with X = H, Me, Et, and O₂N.

Introduction

Covalent halogen nitrates are attracting increasing interest by chemists and atmospheric scientists because of their presence in the atmosphere and their participation in the halogen and NO cycles for ozone depletion in the stratosphere.^{1,2} The geometric structures of the halogen nitrates have a long and controversial history. In 1937 Pauling and Brockway derived from the electron diffraction pattern of FONO₂ a nonplanar structure with the O-F bond perpendicular to the NO₃ plane.³ About 25 years later, IR spectra of FONO₂ and ClONO₂ were interpreted in terms of planar structures.^{4,5} At this time planar structures have also been established for nitric acid, HONO2,6 and methyl nitrate, CH₃ONO₂,⁷ by microwave spectroscopy. Two independent Raman studies of liquid ClONO₂ concluded from polarization data that this nitrate possesses a nonplanar structure of C_s symmetry.^{8,9} On the other hand, similar measurements have been interpreted by other authors in terms of a planar configuration.¹⁰ In 1976 Suenram et al. derived unequivocally from the microwave spectrum a planar structure for ClONO₂,¹¹ The rotational constants of two isotopic species (37Cl and 35Cl), however, did not allow a determination of the geometric parameters. At about the same time, the presence of two rotamers, planar and nonplanar, was deduced from the far-infrared spectrum of the torsional vibration and from a low-resolution microwave spectrum.¹² Ab initio calculations for ClONO₂ have been reported by several laboratories¹³⁻¹⁵ using different levels of theory (HF or MP2) and different basis sets (4-31G, 6-31G*, or Dunning DZP basis). In all cases a planar structure was derived for the ground state. The 6-31G* and DZP basis sets predict very similar geometric parameters. Energy differences between the planar and nonplanar rotamers are predicted to be 80 kcal/mol (HF/ 4-31G),¹³ 6.1 kcal/mol (HF/DZP), and 7.7 kcal/mol (MP2/ DZP).¹⁵ The HF/4-31G value appears to be unreasonably high.

Bromine nitrate has been much less well characterized than its chlorine analogue. The first extensive vibrational study, including IR spectra of the gas, matrix, and solid and Raman data for the solid, has been reported only about 6 years ago by Wilson and Christe.¹⁶ In view of the well established planarity of CIONO₂ at this time, these data were interpreted in terms of a planar configuration for the bromine derivative, as well. The present work reports gas-phase structural studies for CIONO₂ by



Figure 1. Experimental radial distribution function and difference curve for CIONO₂.

the combined use of electron diffraction (ED) intensities and rotational constants from the literature¹¹ and for BrONO₂ based on electron diffraction data alone. In the course of our studies we learned about a high-precision crystal structure determination for chlorine nitrate.¹⁷

Structure Analyses

CIONO₂. The experimental radial distribution curve (Figure 1) can be reproduced only with a planar model. A nonplanar structure with the O-Cl bond perpendicular to the NO₃ plane would possess a strong peak for two O-Cl distances near 3.2 Å and can clearly be excluded. In the joint analysis of ED and microwave data, the molecular intensities were modified with a diagonal weight matrix and known scattering amplitudes and phases were used.¹⁸ A valence force field was derived from vibrational frequencies¹⁶ with the program NORCOR,¹⁹ and this force field was used to calculate vibrational amplitudes and vibrational corrections for interatomic distances ($\Delta r = r_{\rm s} - r_{\rm z}$) and for the rotational constants $(\Delta B^i = B_0^i - B_z^i, B^i = A, B, \text{ or } C)^{20}$ Only constants for the ³⁵Cl species were used in this analysis to avoid systematic errors due to isotopic differences between r_z structures of different isotopic species. The spectroscopic data are collected in Table I, together with the experimental vibrational amplitudes. The relative weight of ED intensities and rotational constants was adjusted, so as to fit the experimental rotational

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[†] Universität Tübingen.

¹ Universität Dortmund.

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TABLE I: Vibrational Amplitudes, Vibrational Corrections, and Rotational Constants (B) for CIONO₂^e

		amplitude			
	distance	ED + MW	spectr	$\Delta r \left(r_{\rm a} - r_{\rm z} \right)$	
N=0	1.19	0.038(2)	0.038	0.0015	
N-O	1.50	0.054(6)	0.062	0.0028	
0-Cl	1.67	0.041(3)	0.051	0.0084	
Oc"Ot	2.19	0.046(8)	0.049	0.0043	
0.0	2.19		0.061	0.0099	
00	2.32	0.052(13)	0.061	0.0009	
NCl	2.63	0.065(8)	0.068	-0.0004	
Cl-Oc	2.74	0.086(12)	0.092	-0.0015	
Cl-O _t	3.67	0.076(9)	0.063	-0.0007	
	$B_0^i(\text{expt})^b$		$B_z^i(expt)$		
A	12106.77(40)) 1215	0.5(44)	12150.5	
B	2777.03(2)	278	5.8(9)	2785.7	
С	2258.11(1)	226	6.1(8)	2266.2	

^a Distances and amplitudes in angstroms; rotational constants in megahertz. ^b From ref 11.

 TABLE II:
 Geometric Parameters for ClONO2 from ED +

 MW, X-ray, and ab Initio Calculations

	ED + MWª	X-ray ^b	HF/ 4-31G¢	HF/ 3-21G*d	HF/ 6-31G*e	MP2/ 6-31G**
N=O _t	31 194(1)	1.2023(7)	1.193	1.212	1.172	1.206
N-=-O _c	y ^{1.1,y} (1)	1.1874(8)	1.197	1.212	1.172	1.202
N0	1.496(3)	1.4698(7)	1.443	1.464	1.372	1.547
0Cl	1.665(2)	1.6838(6)	1.765	1.684	1.666	1.701
N-0-Cl	113.0(3)	112.47(4)	116.3	113.8	115.7	111.1
$O-N=O_t$	108.8(2)	109.33(5)	111.8	110.5	110.7	107.6
0-N-0c	118.6(3)	118.36(5)	116.1	118.4	118.6	117.3
0-N-0	132.6(5)	132.31(6)	132.1	131.1	130.7	135.1

^{*a*} r_{α} structure, error limits are 2σ values. ^{*b*} r_{α} structure from ref 17. ^{*c*} r_{e} structure from ref 13. ^{*d*} r_{e} structure, this work. ^{*e*} r_{e} structure from ref 14.



Figure 2. Experimental radial distribution function and difference curve for BrONO₂.

constants to within their estimated uncertainties (these uncertainties are set to 10% of the corrections ΔB^i). The two N=O bonds, N=O_c and N=O_t, were assumed to be equal in this analysis. This assumption is justified by the ab initio calculations which predict equal or nearly equal values for the two bond lengths, depending on the calculational level. The final results are given in Table II together with the data from the X-ray analysis and from various ab initio calculations.

BrONO₂. Again, the experimental radial distribution function (Figure 2) is compatible only with a planar conformation. If we assume equal N=O double bond lengths, six parameters are required to describe the geometric structure, and these are well determined by the six peaks in the radial distribution function. The areas of the individual peaks in the calculated and experimental functions differ somewhat, the experimental area of the 2.3 Å peak being too large and that of all others slightly too small.

TABLE III: Results of ED Analysis for BrONO₂

				-		-	
		Geo	metric	Paramete	ersa		
N=0) 1.20)5(3) (p ₁)	0-N=	<u>с</u>	119.5(6)	(p ₄)
N-0	1.45	7(5)	$p_2)$	0-N=(D,	106.6(5)	(p ₅)
O-Br	1.82	9(4) (p ₃)	0 — N≃	=O	133.9(8)	
				N-O-B	r	113.9(5)	(p ₆)
<u> </u>	Interat	omic Dista	nces ar	d Vibrati	onal Ar	nplitudes	
	distance	amplitude	;		distanc	e amplitude	
N=0	1.21	0.050(4)	(a ₁)	O.O.	2.14	2	
N-0	1.46	0.047(10)	(a_2)	0O	2.30	30.055	
O-Br	1.83	0.064(5)	(a_3)	N-Br	2.76	0.067 ^b	
Oc••Ot	2.22	0.026(20)	(a ₄)	BrOc	2.86	0.114(13)	(a5)
			,	Br.O	3.80	0.094(12)	(a.)

^a r_a distances and \angle_{α} angles. Error limits are 2σ values and include a possible scale error of 0.1%. ^b Not refined.

This mismatch of the areas disappears if 6% Br₂ is added to the calculated function.²¹ Assumptions for the vibrational amplitudes are evident from Table III. The amount of impurity and the vibrational amplitude used for Br₂ have a strong effect on the vibrational amplitude of the O_c. O_t distance. The least squares analysis of the molecular intensities was performed analogously to that described above. Four correlation coefficients have values larger than |0.5|: $p_4/p_6 = -0.75$, $p_4/a_5 = -0.59$, $p_5/a_4 = 0.51$, and $p_6/a_5 = 0.53$. Numbering of the geometric parameters p_i and the vibrational amplitudes a_k and the final results are given in Table III.

Discussion

The experimental gas-phase structures, which were derived for the two nitrates in this study, are of special interest in comparison to (1) the crystal structure of ClONO₂, (2) ab initio calculations of ClONO₂, and (3) the gas-phase structures of other covalent nitrates. Only very few compounds have been studied with high accuracy in the gas and solid phases, which provide information about the systematic differences of gas-phase and crystal structures. Such differences can be due to steric or electronic interactions in the crystal and/or due to lattice vibrations. The effect of disorder can probably be neglected in the present case. The bond angles in ClONO₂ which are expected to be most effected by steric interactions in the crystal differ by no more than 0.5° from the gas-phase values. The two N=O bonds in the crystal differ slightly, but their mean value (1.195 Å) is in perfect agreement with the gas-phase result (1.194(1))Å). The N-O and O-Cl bond lengths, however, differ considerably, the former being shorter by 0.026 Å and the latter longer by 0.019 Å in the crystal. Such differences between gas-phase and crystal structures may arise from different effects. Whereas ED measures internuclear distances, X-ray crystallography measures distances between maxima of electron densities. In the nitrate we expect that the oxygen lone pairs shift the maximum of the oxygen charge density away from nitrogen, which would lead to a longer N-O bond in X-ray crystallography. The opposite trend, however, is observed. Lattice vibrations may affect bond distances in the solid phase, but the low temperature at which the X-ray data were collected (100 K) and the magnitude of the anisotropic displacement coefficients indicate that this effect is small in the present case. Thus, the different bond lengths result most likely from a variation in the electronic structure, caused by internuclear interactions in the solid, although no unusually short contacts between neighboring molecules are present in the crystal. This interpretation is supported by the vibrational frequency which Wilson and Christe¹⁶ assign to the N-O vibration and which increases from 434 cm⁻¹ in the gas phase to 454 cm⁻¹ in the solid.²² The observed bond length differences can be rationalized straightforwardly by a higher contribution of the ionic structure Cl⁺NO₃⁻ in the solid compared to the gas phase. This makes the N-O bond shorter and the O-Cl bond longer. As

TABLE IV: Geometric Parameters of Nitric Acid and Covalent Nitrates

	HONO2 ^a	CH ₃ ONO ₂ ^b	EtONO2 ^c	BrONO2 ^d	ClONO2 ^d	O2NONO2"
N-0	1.406(3)	1.402(5)	1.405(4)	1.456(5)	1.499(3)	1.495(4)
N=O. N=O.	1.210(3) 1.203(3)	1.205(5) 1.208(5)	} 1.207(3)	1.205(3)	1.1 96(1)	1.186(2)
0-X	0.959(5)	1.437(5)	1.443(4)	1.829(4)	1.673(2)	1.495(4)
N-O-X	101.9(5)	112.7(3)	113.0(6)	113.9(5)	113.0(3)	111.8(16)
0–N – 0°	116.1(3)	118.1(3)	118.2(7)	119.5(6)	118.6(3)	2112 4(8)
$O-N=O_t$	113.9(3)	112.4(3)	112.2(10)	106.6(5)	108.8(3)	§ 113.4(3)
O-N-Ó	130.0(5)	129.5(5)	129.6(17)	133.9(8)	132.6(5)	133.2(6)

 $a r_{s}$ structure from ref 27. $b r_{s}$ structure from ref 28. $c r_{s}$ structure of the anti form from ref 29. $d r_{s}$ structure from this study. $e r_{s}$ structure from ref 30. The NO₂ groups perform large amplitude vibrations around the N-O bonds.

an alternative explanation, ClONO₂ can be regarded to be an adduct of the two radicals ClO[•] and [•]NO₂ which is weaker in the gas than in the solid state. A similar trend was observed for O₂NNO₂, where the N–N bond in the gas phase (1.782(4) Å ²³) is longer than that in the crystal (1.7561(9) Å from neutron diffraction at 20 K ²⁴ and 1.759(2) Å from X-ray diffraction at 228 K ²⁵). This latter bonding model, however, rationalizes the trend in the N–O bond length but does not provide a straightforward explanation for the differences in the O–Cl bond length.

To complement the ab initio calculations reported in the literature, we performed calculations at the HF/3-21G* level, which, according to our experience, in many cases give good agreement with experimental structures. These calculations were performed with the GAUSSIAN 86 program system.²⁶ The calculated geometric parameters are compared with the experimental values in Table II. The theoretical bond lengths exhibit the well-known trends, i.e., slight shortening with increasing basis sets and slight lengthening with inclusion of electron correlation effects, except for the N-O single bond. The predicted value for this bond distance depends drastically on the computational level, and none of the "standard" ab initio methods reproduces the experimental gas-phase value reasonably well. The closest agreement for all geometric parameters is obtained with the HF/ 3-21G* method. Apparently, the errors due to the various approximations in this low-level method cancel each other more than in the other two methods.

Table IV compares the geometric parameters of nitric acid with those of covalent nitrates, XONO₂, whose structures have been determined in the gas phase. The structure of the NO_2 group changes very little with different substituents X. With increasing electronegativity of X a slight shortening of the N=O bonds and widening of the O=N=O angle is observed. The tilt of the NO₂ group relative to the N–O bond, $1/2[(O-N=O_c) (O-N=O_t)$], increases with the increasing size of X from 1.1° in HONO₂ to 6.5° in BrONO₂, reflecting the steric requirement of the substituents. By far the largest variation occurs for the N-O single bond. Whereas this bond length is constant for X = H, Me, and Et, it increases strongly in the halogen nitrates and in N₂O₅ with increasing electronegativity of the substituent. In $ClONO_2$ this bond is nearly 0.1 Å longer than that in nitric acid. This increase in bond lengths is also reflected qualitatively in the frequencies of the N-O vibrations¹⁶ which are considerably lower in the halogen nitrates (394 cm⁻¹ in BrONO₂ and 434 cm⁻¹ in ClONO₂) than in nitric acid (647 cm⁻¹). Of course, these vibrational frequencies also depend on the mass of X and on the degree of mixing with other vibrations. A quantitative relationship between bond length and bond strength would require the determination of force constants.

The dissociation energies XONO₂ \rightarrow XO + NO₂ for the halogen nitrates ClONO₂ (108.6 kJ/mol) and BrONO₂ (88.2 kJ/mol) are considerably smaller than that of nitric acid (206.5 kJ/mol),³¹ correlating qualitatively with the N-O bond lengths as well. Whereas the N-O bond in ClONO₂ is the longest such bond in covalent nitrates, whose structures have been determined, the O-Cl bond is shorter than in most other compounds studied in the gas phase: $r_s = 1.7004(20)$ Å in OCl₂,³² $r_s = 1.6895(35)$ Å



Figure 3. Experimental (O) and calculated (-) molecular intensities and differences for ClONO₂.



Figure 4. Experimental (O) and calculated (-) molecular intensities and differences for BrONO₂.

in HOCl,³³ $r_a = 1.679(3)$ Å in CF₃OCl,³⁴ and $r_a = 1.674(19)$ Å in CH₃OCl.³⁵

Surprisingly, so far no gas-phase structures of compounds containing O-Br bonds have been reported in the literature, except an r_0 structure for the Br-O radical (1.7213 Å ³⁶) which is, of course, not comparable to that in the nitrate. The O-Br bond length derived for BrONO₂ (1.829(4) Å) corresponds almost exactly to the value predicted by the Schomaker-Stevenson rule, which is 1.824 Å.³⁷

Experimental Section

Among the numerous synthetic routes for the preparation of chlorine nitrate, the method described by Schmeisser et al.³⁸ appears to be the most simple one. Furthermore, it results in an almost pure product. Bromine nitrate was prepared according to the method of Wilson et al.¹⁶ by reacting the chlorine derivative with bromine: $2CIONO_2 + Br_2 \rightarrow 2BrONO_2 + Cl_2$. Limitation of the reaction time to 1 h reduces decomposition of bromine nitrate. Continuous separation of Cl₂ increases the yield of BrONO₂ to more than 50% relative to Br₂. A reflux condenser cooled to -35 °C was used for the extraction of Cl₂. The sample was purified by fractional condensation and its purity was checked by IR spectra. Apparently, the small content of Br₂ which was detected in the ED analysis remained from the synthesis.

The electron diffraction intensities were recorded with a Balzers gas diffractograph³⁹ at two camera distances (25 and 50 cm) with an accelerating voltage of ca. 60 kV. The electron wavelength was determined from ZnO diffraction patterns. The sample reservoir was cooled to -50 °C (ClONO₂) and -22 °C (BrONO₂). The inlet system and nozzle were kept at room temperature. The photographic plates were analyzed by the usual procedures⁴⁰ and the averaged molecular intensities in the s-ranges of 2-18 and 8-35 Å⁻¹ in steps of $\Delta s = 0.2$ Å⁻¹ are presented in Figures 3 and 4.

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Supplementary Material Available: Table of numerical values of experimental scattering intensities (4 pages). Ordering information is given on any current masthead page.

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