SPECTROSCOPIC STUDIES OF THIAZYL BROMIDE, NSBr

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ABSTRACT

The He(I) photoelectron and low resolution infrared spectra of thiazyl bromide have been recorded. A new route to this elusive molecule has been developed using thiazyl chloride as the precursor. The first ionisation energy of thiazyl bromide, predicted to arise from excitation of an essentially non-bonded electron localised mainly on the nitrogen and bromine atoms, occurs at 10.45 eV, in good agreement with ab initio SCF calculations. The gas phase Fourier transform infrared spectrum of the new molecule shows a strong band at 1311 cm⁻¹, the ν_1 N-S stretching fundamental. Calculations have also been carried out on thiazyl fluoride and thiazyl chloride.

INTRODUCTION

The spectroscopy of molecules of general formula ABC, where A is a group V element, B is a group VI element and C is a halogen has been of interest for some time. The nitrosyl halides XNO, where X = halogen, have been the subject of extensive study by microwave [1], infrared [2,3] and photoelectron spectroscopy [4-7]. They are bent triatomic molecules of structure X-N=O and show instability and high reactivity, being decomposed by visible light or by contact with metals. However, the analogous series of sulphur compounds have the general structure X-S=N with angle X-S=N approximately 120° . Thiazyl fluoride has been the subject of several photoelectron studies [8–10] the latter one also including thiazyl chloride. Infrared spectroscopic studies have been carried out on these molecules, using matrix isolation [11-13], and low resolution gas phase techniques [14–16]. In all of these studies, work has focused on NSF and NSCI with only a single report of the observation of NSBr [13]. Recently the photoelectron and matrix isolation spectra of the related molecules CIPO and CIPS have been reported [17] and also mass spectra of BrPO [18].

With the intention of measuring the infrared spectra of these molecules under high resolution (0.004 cm^{-1}) , we have repeated the preparation of NSCl and attempted to prepare NSBr as reported in ref. 13. We have been unable to

observe spectra assignable to NSBr using the previously reported method and have thus devised an alternative route. It may be that the lifetime of NSBr is very short at room temperature and that its generation from the $S_4N_3^+Br^-$ precursor is slow [19].

EXPERIMENTAL

The first stage in the synthesis of thiazyl chloride required the preparation of thiodithiazyl dichloride, $S_3N_2Cl_2$ followed by reaction of this material with more disulphur dichloride to yield thiotrithiazyl chloride, S_4N_3Cl [20]. The sample of $S_3N_2Cl_2$ had a melting point of 91° [90°–92° in ref. 20] and its infrared spectrum was obtained as a KCl disc showing strong bands at 3138, 1407, 1013, 700 and 485 cm⁻¹. S_4N_3Cl had a melting point of 182° [180°–200° in ref. 20] and showed infrared bands at 1165, 1001, 683, 565 and 469 cm⁻¹ in a KCl disc, these values being in good agreement with previous work [21]. Following the method of Peake and Downs [13], S_4N_3Cl was converted into S_4N_3Br , a bright orange solid. This material was dried and transferred to a small furnace attached to a flow cell in the sample compartment of the infrared spectrometer. The sample was carefully warmed and the gases evolved were passed through the cell. No bands assignable to NSBr were obtained.

The next stage involved converting $S_3N_2Cl_2$ into trithiazyl chloride, $S_3N_3Cl_3$ according to ref. 20. This yielded a pale yellow solid with a melting point of 75° before recrystallisation (literature 75°) and showed bands in the infrared spectrum at 3138, 3045, 2814, 1762, 1407, 1011, 699 and 484 cm⁻¹. Thiazyl chloride may be easily generated from $N_3S_3Cl_3$ by gentle heating to 80–85° and its spectrum obtained by flowing directly into the spectrometer. If instead, the thiazyl chloride is passed over potassium bromide heated to 900–950 K, thiazyl bromide is produced, which is then pumped into an infrared gas cell or into the ionisation region of the photoelectron spectrometer.

The infrared spectra were obtained on a Perkin–Elmer 1720 FTIR spectrometer at a resolution between 4 cm⁻¹ and 0.5 cm⁻¹ using a 15 cm path length infrared flow cell fitted with KBr windows and the photoelectron spectra were taken on a purpose built fast pumping instrument. The resolution was typically 25 meV and the spectra were calibrated with Argon and known byproducts.

COMPUTATIONAL DETAILS

In order to assist in the assignment of the photoelectron spectrum of NSBr, we have carried out ab initio SCF molecular orbital calculations on NSF, NSCI and NSBr. The calculations used double-zeta basis sets and were carried out at the experimental equilibrium geometries of these molecules. For N and F we used Dunning's 4s2p basis sets [22]; for S and Cl we used Dunning and

Hay's 6s4p bases [23], with the chlorine basis modified according to Craven et al. [24]; and for Br we used Dunning's 8s6p2d basis, given by Bauschlicher et al. [25]. The precise geometries we used are as follows: for NSF: r(N-S) = 1.446 Å, r(S-F) = 1.646 Å, $\theta(NSF) = 117^{\circ}$ [26]; for NSCl: r(N-S) = 1.450 Å, r(S-Cl) = 2.161 Å, $\theta(NSCl) = 118^{\circ}$ [13], and for NSBr: r(N-S) = 1.450 Å, r(S-Br) = 2.260 Å, $\theta(NSBr) = 122^{\circ}$ [13].

The calculations gave energies of -551.17795, -911.20900, and -3024.07366 a.u. for NSF, NSCl, and NSBr, respectively. The ionisation energies were estimated by Koopmans' theorem [27]. Earlier calculations on NSF [28,29,9,10] and NSCl [10] indicate that this approximation gives a reasonable account of the electronic structure of these molecules. Apart from the usual overestimation of the ionisation energies by about 10% [27], the major error is the incorrect ordering of the 6a' and 2a'' valence orbitals. All calculations were carried out using the HONDO program [30].

RESULTS AND DISCUSSION

The spectrum shown in Fig. 1(a) is the infrared spectrum of thiazyl chloride and within the range of the spectrometer used, two fundamental vibrations ν_1 (N=S stretching) and ν_3 (S-Cl stretching) were observed. The values of 1326 and 414 cm⁻¹, taken as the band centres are in good agreement with previous work [16]. Under certain conditions bands due to HNSO [31] and SO₂ [32]



Fig. 1. (a). The infrared spectrum of NSCl. Fig. 1 (b). The infrared spectrum of NSBr.

were present, as decomposition products, at 1257 and 1361 cm⁻¹, respectively. The spectrum shown in Fig. 1(b) is the result of passing thiazyl chloride over heated potassium bromide. It is clear that the band in NSCl at 1326 cm⁻¹ has disappeared and a new feature centred at 1311 cm^{-1} has appeared. This value is in good agreement with the previously reported value of 1312 cm^{-1} for thiazyl bromide, NSBr [13]. This is the only fundamental band expected to lie within the range of the spectrometer.

Having confirmed the presence of thiazyl bromide by IR spectroscopy we next obtained the He(I) photoelectron spectrum of this molecule. This is shown in Fig. 2(b) with the spectrum of thiazyl chloride shown above it in Fig. 2(a) for comparison. In Table 1 we show the experimental and calculated valence i.e.s and orbital symmetries of NSF, NSCl and NSBr.

In Fig. 3 we show contour plots of the six highest valence orbitals of NSBr These were obtained with Purvis's QUIPU program [33]. For all orbitals, the



Fig. 2 (a). The He(I) photoelectron spectrum of NSCl. Fig. 2 (b). The He(I) photoelectron spectrum of NSBr.

TABLE 1

	Experimental	Calculated	Orbital symmetry
NSF ^a	11.82	12.75	7a'
	13.50	14.57	2 a "
	13.87	15.31	6a'
	15.61	18.22	5a'
	16.56	19.01	1 <i>a</i> "
	17.24	19.14	4a'
	21.11	23.95	3a'
		36.61	2a'
		44.21	1 <i>a'</i>
NSCI⁵	10.96	11.27	7a'
	11.80	12.48	2a″
	11.80	12.71	6 <i>a'</i>
	13.77	15.92	1 <i>a</i> ″
	14.46	16.19	5 a ′
		17.25	4 <i>a</i> ′
		22.95	3 a ′
		30.18	2a'
		37.12	1a'
NSBr	10.45	10.67	7a'
	10.85	11.60	2 <i>a</i> ″
	11.09	11.80	6a'
	12.87	15.66	1 <i>a</i> "
	13.45	15.95	5a'
		17.00	4α΄
		22.60	3a'
		28.47	2a'
		36.84	1a'

Vertical ionisation energy (eV)

^aRef. 28. ^bRef. 10.

contour value used is 0.1 e/Å³, as recommended [33]. For clarity, different orientations of the molecule have been used to display a' and a'' orbitals.

Our thiazyl chloride spectrum is in good agreement with that obtained previously [10], there being four bands, the second of which is of greater width and accounts for two ionisations. The semi-empirical extended Hückel theory calculations of Cowan et al. [10] predict the ordering of the first five orbitals to be, in order of increasing i.e., 7a'6a'2a''5a'4a', while our ab initio calculations give the order 7a'2a''6a'1a''5a'. While neither calculation can be expected to be definitive, we would be surprised if the 4a' orbital had a lower i.e. than the 1a'' orbital, as this would imply that our estimate of the difference of the i.e.s of these orbitals was in error by over 1.3 eV. On the other hand, it is quite possible that our ordering of the i.e.s of the nearly degenerate 2a'' and 6a' orbitals is incorrect. We note at this point that the assignment of the or-



Fig. 3. Contour plots of the first six valence orbitals of NSBr, as calculated with a DZ basis set SCF wave function.

bitals of NSCl on the basis of the assignments for NSF [10] is somewhat dubious, owing to the different nature of the orbitals of the two molecules. We return to this point later when discussing correlation diagrams for the thiazyl halides.

Examining the spectrum of thiazyl bromide shown in Fig. 2(b) in more detail, it can be seen that the spectrum bears a strong resemblance to that shown above in Fig. 2(a), except that the bands have been shifted to lower i.e., to a larger or smaller extent. Our calculations predict the first three ionisations to be separated by only 1.13 eV and for the order to be $a'(\sigma)$, $a''(\pi)$ and $a'(\sigma)$. In the case of thiazyl chloride the order is predicted to be the same and these ionisations are calculated to be spread over 1.44 eV. In the spectrum of thiazyl bromide the first two ionisation bands are quite sharp and have vertical i.e.s of 10.45 eV and 10.85 eV. There is a shoulder on the high energy side of the second band, the maximum of which is difficult to discern, but is probably close to 11.10 eV. The first band at 10.45 eV is associated with ionisation from essentially non-bonding N and Br orbitals and would be expected to move to lower i.e. when the less electronegative bromine atom takes the place of the chlorine atom. The same effect is predicted for the next two orbitals which are both halogen lone pairs. The next region of ionisation in the spectrum starts at approximately 12.5 eV and contains two main bands, the first with a maximum at 13.00 eV and the second at 13.45 eV. These are associated with nitrogen-sulphur $a''(\pi)$ and nitrogen-sulphur $a'(\sigma)$ bonding orbitals.

The ionisation energies of thiazyl bromide are compared to those of thiazyl chloride [10] and thiazyl fluoride [8,9] in the correlation diagram shown in Fig. 4. Also shown are the positions of the first band and regions of the second and third bands of NS [34]. The first band is known with some degree of accuracy, but owing to the plethora of states produced on ionisation of the second and third orbitals (ten ionic states in all) only an estimate was given for these, 12.5-13.5 eV. However the general picture follows that observed previously for the series XNO [4] vis, a distinct division of the bands into two regions, separated by several electron volts, but less than that observed for the



Fig. 4 (a). Correlation diagram of the calculated ionisation energies of the thiazyl halides. Fig. 4 (b). Correlation diagram of the experimental ionisation energies of the thiazyl halides and the thiazyl radical.

XNO series. This may be taken to indicate a stronger interaction between the X and NS groups than is the case for XNO. The as yet unobserved iodide would be expected to have similar ionisation energies to the bromide, shifted to slightly lower energy.

The fluoride, because of fluorines' more tightly held valence electrons, has a somewhat different electronic structure to the chloride and bromide, although there is a strong similarity between the i.e.s of NSF and those of NSCl and NSBr. Thus, the 2a'' and 6a' orbitals of NSF are strongly N-S Π bonding and S-F antibonding, whilst in NSCl and NSBr these orbitals of NSF have substantial fluorine lone pair character, while the corresponding orbitals in NSCl and NSBr are mainly N-S bonding orbitals. It follows that it is not meaningful to connect the NSF and NSCl energy levels in the correlation diagram, although the progression from fluoride to chloride parallels that from chloride to bromide.

Finally, we note that earlier calculations on NSF suggest the formulation N=S-F [28]. Our own calculation on NSF is in accord with this and our data suggests this also for NSCl and NSBr.

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