

Journal of Molecular Structure 408/409 (1997) 161-169



Substituted oximes and furoxans as precursors to unstable nitrile oxides. Electronic and geometric structures by ultraviolet photoelectron spectroscopy, infrared spectroscopy and ab initio calculations

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Received 26 August 1996; accepted 6 September 1996

Abstract

The relationship between dihaloformaldoximes and disubstituted furoxans as transient nitrile oxide generators in the gas phase is discussed. HeI photoelectron and mid-infrared spectroscopy are used, for the first time, to obtain spectra of the oxime and furoxan precursors, and of the thermolysis products, the substituted nitrile oxides. Assessment of the structures for these three apparently disparate groups of compounds is assisted by conventional ab initio calculations, and also by calculations employing density functional theory. © 1997 Elsevier Science B.V.

Keywords: Oximes; Furoxans; Nitrile oxides; Spectroscopy; Theory

1. Introduction

We have recently been investigating the chemistry and spectroscopy of transient nitrile oxides XCNO (X = $Cl - , Br - , H_3C - , NC - and ONC -)$ generated into the dilute gas phase. In general, although not exclusively, the stable dihaloformaldoximes, XYC=NOH (X, Y = halogen) and the stable disubstituted furoxans (1,2,5-oxadiazole 2-oxides) can both act as suitable precursors to nitrile oxides. Scheme 1 shows this relationship.

Our principal interests are in the structures (linear, bent or quasilinear) and spectroscopy of the unstable XCNO species. Scheme 1 shows that routes to these interesting 1,3-dipolar species can be achieved via HX elimination from X_2 CNOH (thermolysis or base), or by thermolytic cycloreversion of the corresponding furoxans. In addition, the nitrile oxides themselves can rapidly dimerise to the corresponding furoxans.

This account considers the relationships between these three quite different types of molecules, and the representative spectroscopy of each class with particular emphasis on the electronic and geometric structures investigated by spectroscopy [UV photoelectron (PE) and FTIR] and ab initio methods. We will first discuss the apparatus, and synthetic/ generation procedures, followed by the structures and spectroscopy of the three classes of compounds.

We should point out that to investigate successfully transient nitrile oxides in the gas phase requires a broad band detection technique that can follow the

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on-line chemistry. The chemistry, whether it be thermolysis, gas-solid reaction etc. can then be tuned for optimum yields, and the experience gained can then be applied to other, more specific gas phase techniques such as FTIR or microwave spectroscopy.

2. Experimental

2.1. Spectroscopic methods

The principal apparatus (Fig. 1) consists of a homebuilt fast pumping HeI PE spectrometer used to monitor, in situ, the products of thermolysis reactions. A unique feature of this instrument is that it is not in a large vacuum chamber, but instead is pumped directly from below. This means that the distance from molecule generation to ionisation can be made very short. The spectrometer can also mass analyse ions produced in the photoionisation process (PIMS) using a quadrupole mass analyser (Hiden Analytical, 320 amu), with its electron impact source removed, mounted directly above the photoionisation point. Single wavelength PIMS spectra are obtained with HeI (21.22 eV) or unfiltered HL_{α,β,γ} (10.2–12.7 eV) radiation. PE and PIMS spectra can be recorded within seconds of each other, of much benefit in the identification of transient and new gas-phase species.

IR spectra, at 0.5 cm⁻¹ resolution, were collected on a Nicolet 20SXC interferometer using a 20 cm single pass gas cell with KBr windows. The effluent from the pyrolysis or reaction tube was pumped continuously



Fig. 1. The combined ultraviolet photoelectron (PE) and photoionization mass (PIMS) spectrometer used for on-line spectroscopy of unstable molecules, in this case by thermolysis over quartz chips.

through the cell, whilst maintaining the pressure constant, typically between 200 and 500 mTorr. Raman spectra of the crystalline stable precursors were recorded, using Nd:YAG excitation (1.064 μ m), on a Bruker RFS 100 FT-Raman spectrometer at 2 cm⁻¹ resolution, and a laser power of 100 mW.

2.2. Synthesis of oximes and furoxans and generation of nitrile oxides

The dihaloformaldoximes were synthesised using literature methods. Cl₂CNOH was prepared by reduction of trichloronitromethane with tin metal [1]. Br₂CNOH was synthesised from oximinoacetic acid and bromine [2], and BrClCNOH was obtained from Br₂CNOH and mercuric chloride [3].

Disubstituted furoxans were prepared by a variety of methods. Dibromofuroxan was prepared according to Scheme 1; that is BrCNO was generated from dibromoformaldoxime, and this was then trapped and revaporised as the furoxan dimer [4]. Dicyanofuroxan was synthesised from cyanoacetic acid using the literature method [5], and dichlorofuroxan was obtained from dichloroglyoxime [6] (prepared from glyoxime and chlorine). Dimethylfuroxan was prepared by a new method, the oxidation of dimethylglyoxime with conc. nitric acid [7].

All of the nitrile oxides discussed herein were made into the gas phase by either of the procedures shown in Scheme 1. For ONCCNO, dichloroglyoxime was used, this turning out to be a very clean route, the only other product being HCl [8], although ONCCNO can also be obtained in lesser yield by thermal Br₂ elimination from the dibromofuroxan dimer [8]. Both NCCNO [9] and H₃CCNO [7] are generated, essentially quantitatively, from their furoxan dimers. The halogenated species are more troublesome, the thermolytic cycloreversion of the disubstituted furoxans leading to other products, e.g. ONCCNO, vide supra. Both BrCNO and ClCNO are best made by HX elimination from their respective dihaloformaldoxime species [4,7]. Direct thermolysis, using the apparatus of Fig. 1 is entirely feasible, but side-products, especially HX, X₂, and NO, are also observed. Thermolysis over metals, e.g., Cu at 350°C in the case of CICNO, or reaction with base, e.g., titration of $Br_2CNOH(g)$ with $NH_3(g)$ in the case of BrCNO is also feasible.

2.3. Computational methods

Ab initio calculations were carried out using either Gaussian-92 or Gaussian-92/DFT [10]. The basis sets used varied from system to system (see below), but were generally 6-31G^{*} or better, and correlation in the form of Møller-Plesset, MPn (n = 2-4) was used whenever possible. For cases involving bromine, a basis set of [6s4p2d] quality on bromine [11] was used. In some cases, especially with bromine present, the core electrons were not included in the correlation energy calculations (i.e. "frozen-core"). Equilibrium molecular geometries were fully optimised and harmonic vibrational frequencies were then calculated at the minima using numeric second derivatives. With DFT we employed the B3-LYP exchange-correlation functional. All calculations were performed on a Silicon Graphics Challenge/XL workstation.

3. Structures:

3.1. Dihaloformaldoximes

For all three species investigated here, $Cl_2C=NOH$, Br₂C=NOH, and BrClC=NOH, there is no spectroscopy or structural data known, despite the fact that such species are used in organic chemistry as precursors for the in situ generation of nitrile oxides, important transient intermediates in 1,3-dipolar cycloadditions.

For the dichloro- or dibromo-compounds there is the possibility of *syn*- or *anti*-hydrogen atoms, and for BrClC=NOH with two different halogen atoms, there is the possibility of four planar conformations, due to the additional opportunity for a Z (*cis*)- or *E* (*trans*)-conformation with respect to the C=N double bond (Scheme 2).

The scheme shows the relative stability decreasing from left to right with Z-a the thermodynamically more preferred over E-a, albeit by only 2.4 kJ mol⁻¹.

MP2(fc)/ $6-31G^{**}$ calculations for the three dihalospecies indicate planar structures with, in all cases, both *syn*- and *anti*-conformers having stable minima. With respect to the CN double bond, both the *E*- and *Z*-isomers also have stable minima. The equilibrium structures are shown in Table 1, together with the calculated total energies, dipole moments and



rotational constants of potential assistance for future structural work. A calculated structure (at the same level of theory) for the known parent molecule H_2 CNOH, for which an experimental structure has been obtained [12], and for which only an *anti*-structure is observed, gives some confidence that the calculated structures for the dihalo-species are quite reasonable. Dihalo-substitution does not influence the C=N double bond, but slightly shortens the N– O bond, and increases the angle at nitrogen from 110° in H_2 CNOH to ca. 112° and ca. 118° for *anti*- and *syn*-structures, respectively.

3.2. Disubstituted furoxans:

The parent furoxan $H_2C_2N_2O_2$ is unknown, and is best described as having an electron-overcrowded

ring [13,14]. Substitution permits delocalisation of this excess charge onto the substituents, thereby stabilising the disubstituted species. Since our interest is in the thermolytic properties of these molecules, the structures are of interest for investigating potential cleavage points in the molecules.

Structural data on many aryl and alkyl substituted furoxans is known [15]. Table 2 shows the experimental bond lengths of the dibromo- [16] and dicyanofuroxans [17] for which we have obtained crystal structures, together with calculated HF, MP2 and B3-LYP structures. The bond lengths and angles in both furoxan substructures generally track those in other substituted derivatives [15], but for dicyanofuroxan, all bonds, except C_4N_5 , are outside the ranges determined from critical analyses of the mean bond lengths of fourteen substituted furoxans of known

Table 1

	Cl ₂ CNOH	BrClCNOH	BrClCNOH	Br ₂ CNOH	
	anti	Z-anti	E-anti	anti	
Х-С	1.716	1.714	1.883	1.880	
Y-C	1.715	1.888	1.714	1.886	
C=N	1.285	1.283	1.284	1.282	
N-0	1.399	1.396	1.400	1.399	
O-H	0.967	0.968	0.968	0.968	
XCN	117.6	118.1	116.9	117.6	
YCN	125.7	125.1	126.1	125.7	
CNO	111.6	112.1	111.6	112.1	
NOH	101.2	101.3	101.1	101.3	
Total energy:	- 1087.376481	- 3197.777234	- 3197.776317	- 5308.177806	
μ^{b}	0.940	0.955	0.877	0.846	
A°	4.3679	2.9625	4.2926	2.8178	
В	2.5701	2.0596	1.5170	1.1617	
С	1.6180	1.2149	1.1209	0.8226	

^a Bond angles in degrees, bond lengths in Å, total energies in a.u.; calculated at the MP2(fc)/6-31G^{**} level.

^b Dipole moment in Debye.

^c Rotational constants in GHz; isotopes ³⁵Cl, ⁷⁹Br, ¹²C, ¹⁴N, ¹⁶O, ¹H.

Table 2 Experimental and theoretical bond lengths in disubstituted furoxans^{a,b}

H H H H H H H H H H H H H H H H H H H		Br N Br ₂ C ₂ N	$ \begin{array}{c} Br & Br \\ c & c \\ N & N \\ Br_2 C_2 N_2 O_2 \end{array} $		NC) 20	N N C C C N O (NC) ₂ C ₂ N ₂ O ₂			14-aryl/alkyl furoxan structures from Ref. [15]			
Bond	Expt.	B3-LYP	Expt.	HF	B3-LYP	Expt.	HF	MP2	B3-LYP	Mean	Lo	Hi
$\overline{N_2 - O_6}$		1.218	1.228	1.207	1.214	1.206	1.192	1.200	1.205	1.234	1.228	1.240
$O_1 - N_5$		1.364	1.359	1.359	1.374	1.354	1.350	1.310	1.351	1.380	1.370	1.388
$O_1 - N_2$	_	1.468	1.438	1.340	1.466	1.454	1.336	1.649	1.476	1.438	1.430	1.447
$N_2 - C_3$	-	1.331	1.299	1.300	1.332	1.344	1.315	1.355	1.345	1.316	1.311	1.324
$C_3 - C_4$	_	1.412	1.40	1.421	1.418	1.401	1.424	1.407	1.430	1.417	1.412	1.422
$C_4 - N_5$	-	1.310	1.25	1.271	1.303	1.300	1.275	1.343	1.314	1.304	1.300	1.308

^a Experimental data for $Br_2C_2N_2O_2$ and $(NC)_2C_2N_2O_2$ are crystal structures [16,17].

^b Calculations are HF/6-31G^{*}, MP2/6-31G^{*}, B3-LYP/6-31G^{*}; bond lengths in Å.



structure [17] (see final three columns of Table 2). This indicates that the structure of dicyanofuroxan is not typical for a furoxan, although the three interconnected N–O bonds still follow the trend, N_2O_6 $< O_1 N_5 < O_1 N_2$. Dibromofuroxan is also atypical and shows short CN bonds. For the ab initio methods, the most important observation is that HF fails in the relative ordering of the lengths of the three interconnected N–O bonds, with O_1N_2 , which is known to be long (and the point of cleavage) calculated shorter than O_1N_5 . MP2 dramatically overcompensates, such that the average MP2 differences from experiment are greater than those of HF. DFT does a reasonable job, being a possible alternative to traditional electron correlation methods (at least in comparison with MP2). The calculated geometries of dicyanoand dibromofuroxan using the B3-LYP/6-31G* method (Table 2) give the best agreement with the solid-state structures. The overall average deviation is a reasonable 0.015 Å and the angles (not shown) are especially well reproduced by the DFT method. The table also includes the calculated structure for the unknown parent furoxan molecule. The cleavage/ dimerisation process itself is clearly also of computational interest.

3.3. Nitrile oxides

We have obtained spectroscopic data for four new nitrile oxides in the gas phase, ClCNO [7], BrCNO [4], NCCNO [9] and ONCCNO [8] (H₃CCNO has been investigated previously [18]). Only one of the four new species has been structurally characterised, NCCNO [19], by microwave spectroscopy.

The principal question here is whether or not such molecules with the formulation, $X-C \equiv N \rightarrow O$ are linear, or bent, or quasilinear. Our ab initio calculations, which in some cases go up to MP4SDQ or QCISD [4,8,9] with or without triples, cannot definitively predict, and neither for that matter can the microwave of NCCNO [19], since vibrational satellites were not observed under the conditions of the pulsed jet, although a linear formulation was deemed the most likely. Although conventional ab initio calculations have done reasonably well for the dihaloformaldoximes, and DFT is shown to be better than HF or MP2 for the furoxans (the nitrile oxide dimers), it is evident that theory has more trouble with the nitrile oxides. The issues really revolve around the basis set size (e.g. our basis sets are probably too small, but we are constrained computationally), the issue of triples favouring bent structures, and indeed the lack of



Fig. 2. Calculated (B3-LYP/6-31G^{**}) bending curves for FCNO (1402), ClCNO (37), BrCNO (0) and NCCNO (0), with the calculated barrier heights in cm^{-1} given in parentheses. For comparison the barrier for HCNO calculated at this level of theory is 0 cm^{-1} .

structures for comparison. Nevertheless, trends are important, and what has become clear is that the substituent has an effect on the calculated barrier such that the NC-substituted nitrile is likely to be linear, whereas the Br and Cl species are likely to be quasilinear, and the F-substituted species is predicted to be bent. These are summarised in Fig. 2, which shows angle bending curves obtained using B3-LYP/6-31G^{**}.

Computationally much remains to be done on these molecules, as has been done in the parent HCNO case, which has been subjected to innumerable calculations [20,21]. In the final analysis, good gas phase structures are required.

4. Spectroscopy

4.1. Dihaloformaldoximes

As mentioned above no spectroscopy has been performed on these molecules. We will focus attention on the infrared and Raman spectra of BrClCNOH as an illustrative example. Hel photoelectron spectra (not shown here) have been obtained, and in a most straightforward way show trends in the dihalo-series, i.e., they provide an analysis of the effect of halogen substitution on the orbitals of the parent oxime species, $H_2C=NOH$ [22].

Fig. 3 shows the spectra obtained for the gas-phase IR and solid-phase Raman. By analogy with the vibrational spectrum of H₂CNOH [23], the first band at 3631 cm⁻¹ is assigned to ν_1 , the OH stretch (such a vibration in free oximes generally occurs in the 3650– 3500 cm⁻¹ region [24,25]), with the next two IR bands at 1602 and 1349 cm⁻¹ originating from the C=N



Fig. 3. BrClC=NOH; infrared (gas) and FT-Raman (solid).

stretch, ν_2 , and the OH in-plane bend, ν_3 , respectively. In the Raman spectrum weak broad bands ascribable to solid-phase OH stretching and bending vibrations are observed around 3200 and 1400 cm⁻¹. Such gassolid shifts are typical for oximes [24–26] representing the difference between free and associated OH.

Two close, strong, IR bands just below 1000 cm⁻¹ are assigned to ν_4 and ν_5 , the NO stretch, and CNO inplane deformation, respectively. The NO stretch in oximes typically appears around 930 cm^{-1} [24], and is weak in the Raman as seen here. The assignment of the more intense band of the two to the CNO deformation is atypical since this fundamental generally appears around 550–600 cm^{-1} , but a potential energy distribution calculated using unscaled ab initio force constants indicates that this mode is strongly coupled with ν_6 , the C(Br)Cl stretch at 640 cm⁻¹. In Cl₂CNOH these two bands are switched. Vibrations associated with the C-X stretches are generally weak in the IR, but below 600 cm^{-1} strong bands in the Raman can be assigned to these modes, although they are strongly coupled with the CNO framework.

One important conclusion to be drawn from the vibrational analysis is that only one isomer is present in the spectrum. From a comparison with ab initio calculated vibrational frequencies it appears that *E-a* (Scheme 2) is the likely isomer [27], and was therefore stereoselectively synthesised, although, as mentioned, the calculated *Z-a* structure is marginally more stable by 2.4 kJ mol⁻¹. As it turns out BrClCNOH selectively eliminates HCl upon thermolysis, giving good yields of BrCNO, thereby lending some support to the *E-a* structure.

4.2. Disubstituted furoxans

We recently reported vibrational data for dicyanofuroxan [17] and find that, unlike the conventional ab initio methods, DFT is of some value for vibrational analysis of both dicyano- and dibromofuroxan. The PE spectra are perhaps more interesting. The PE spectrum of dichlorofuroxan is shown in Fig. 4 with the highest lying levels labelled. Ionisation energy trends in the series of PE spectra with substitution by H₃C-, NC-, Br- and Cl-substituents can be followed fairly smoothly [7]. In general, Koopman's theorem holds for these molecules, apart from the dicyano-species.



Fig. 4. HeI photoelectron spectrum of dichlorofuroxan; the three highest lying levels are labelled, with orbitals arising from mainly Cl 3p above 12 eV.

4.3. Nitrile oxides

The spectroscopy of the nitrile oxides has turned out to be very interesting, not surprisingly given that the parent HCNO molecule has been, and continues to be the subject of intense interest [20,21]. PE and IR spectra have been obtained for all five species, $H_3C -$, NC -, Br -, Cl -, and ONC -, and in the case of the last four, high resolution infrared spectra have been obtained on selected bands [28,29]. For those spectra analysed, B_0 values have been obtained, but as remarked above, definitive structural information must await isotopic investigation.

Typically, in the infrared, the nitrile oxides exhibit strong bands in the 2200 and 1300 cm⁻¹ regions, assignable to the antisymmetric and symmetric stretches respectively. In general the vibrations associated with the substituent are weak, especially in the case of the halogens, Cl – and Br –, and in the special case of ONC-substitution only species of ungerade symmetry are seen due to the centrosymmetric nature of ONCCNO. Fig. 5 shows a detail of the ν_s (CNO) region for three species. These exhibit parallel band type structure as expected for linear molecules, but the corresponding ν_{as} (CNO) mode (not shown) indicates a major issue associated with the analysis of high





Fig. 5. Detail of the ν_s (CNO) region in the gas-phase infrared spectra of ClCNO, BrCNO and ONCCNO.

resolution spectra, namely the presence of strong hot bands in the bending vibrations. In the case of NCCNO the lowest bending mode has been estimated at 86 cm^{-1} from combination bands [28].

The PE data for these molecules gives an account of the valence level structure when a substituent is placed on HCNO. Fig. 6 illustrates just such an orbital scheme for the formation of the orbitals of NCCNO from NC and CNO fragments. This is juxtaposed with the experimental PE spectrum of NCCNO. The resolution of the technique does not permit an unambiguous assessment of the linearity, but degeneracy breaking of the π levels is not observed.



Fig. 6. Orbital scheme for the formation of the molecular orbitals of NCCNO, together with the HeI photoelectron spectrum.

5. Conclusion

We have shown that dihaloformaldoximes are one of the essential ingredients for generating transient nitrile oxides and their stable furoxan dimers, and in some cases, specifically NC – and H_3C –, the furoxan dimers can be thermolytically cleaved to give back, cleanly, the monomers. We have obtained both vibrational and photoelectron data on the oxime and furoxan precursors in addition to the unstable nitrile oxides. Some general comments thus follow. Firstly, it is only by following the spectroscopic changes (using apparatus like that shown in Fig. 1) that one can tune the chemistry for production of the intermediate unstable species. Secondly, trends are important for several reasons, for assigning IR and PE spectra, and for investigating the efficacy of ab initio methods. Thirdly, there are some limitations in the theory that we have applied to assess the likely behaviour of the potentially quasilinear nitrile oxides. Clearly these molecules present an interesting challenge for computational chemistry and, indeed, for their structural determination.

Acknowledgements

N.P.C.W. thanks the Natural Sciences and Engineering Research Council of Canada (NSERC) for operating and equipment grants in support of this work. T.P. thanks NSERC for the award of a NATO Science Fellowship.

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