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Electronic structure and tautomerism of thioamides

Igor Novak^{a,*}, Leo Klasinc^b, Sean P. McGlynn^c^a Charles Sturt University, POB 883, Orange, NSW 2800, Australia^b Physical Chemistry Department, Ruđer Bošković Institute, HR-10002 Zagreb, Croatia^c Louisiana State University, Baton Rouge, LA 70803, USA

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ABSTRACT

The electronic structures of several thioamides have been studied by UV photoelectron spectroscopy (UPS). The relative stabilities of keto–enol tautomers have been determined using high-level ab initio calculations and the results were used in the analysis of UPS spectra. The main features of electronic structure and tautomerism of thioamide derivatives are discussed. The predominant tautomers in the gas phase are of keto–(thio)keto form. The addition of cyclohexanone moiety to the thioamide group enhances the Lewis base character of the sulfur atom. The addition of phenyl group to the (thio)amide group significantly affects its electronic structure.

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1. Introduction

Thioamides are carboxylic acid derivatives which are important reagents and catalysts in organic synthesis and medicinal chemistry [1–3]. Thioamides which can be prepared by Willgerodt–Kindler reaction (which uses elemental sulfur) are useful as building blocks for the synthesis of biologically relevant heterocyclic scaffolds. Thioamides exhibit many interesting properties. They are stronger hydrogen donors (via sulfur atom) and weaker hydrogen bond acceptors than the corresponding amides. In addition, when compared to amides and formamides, thioamides possess different bond-lengths and bond-rotation characteristics. These unique properties have been exploited in both medicinal and polymer chemistry applications. Thioamides are used as catalysts in asymmetric cooperative proton transfer reactions. The most important property of thioamides is the soft Lewis base character of sulfur atom which can be activated by soft Lewis acid/hard Brønsted base pair in the mode of cooperative catalysis (Scheme 1).

The thioamide group can thus act as (pro)nucleophile and electrophile within the same catalytic mechanism.

The Lewis acid/base properties of sulfur and nitrogen atoms of the thioamide group can be expected to be directly related to the electronic structure of the thioamide group e.g. to the electron donating/accepting abilities of the two heteroatoms (Scheme 1). We therefore investigated the electronic structure of substituted

thioamides which contain a cyclohexanone substituent. The presence of cyclohexanone ring can be expected to stabilize enol tautomers B and D (through resonance delocalization between C=C and C=X groups) as shown in Scheme 2. The presence of stabilizing intramolecular hydrogen bonding in tautomers A, B and D is also possible. We shall use UPS data to determine the presence of the most abundant tautomer.

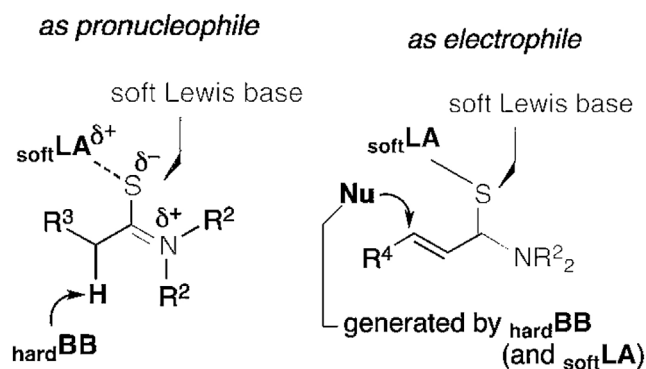
2. Experimental and computational methods

The samples of the compounds studied were prepared according to the reported procedures [4]. The HeI photoelectron spectra (UPS) were recorded on the Vacuum Generators UV-G3 spectrometer and calibrated with small amounts of Xe gas or HBr which was added to the sample flow. The resolution in HeI spectra was 30 meV when measured as FWHM of the $3p^{-12}P_{3/2} Ar^+ \leftarrow Ar ({}^1S_0)$ line. The samples were studied with the inlet probe temperatures between 60 and 160 °C. The spectra obtained were reproducible. Signs of some decomposition were detected in the spectra of **3** and **4**. Decomposition is usually demonstrated by the appearance of sharp peaks which are due to the presence of small molecules/decomposition products in the spectrometer's ionization chamber. The decomposition peaks were of low intensity which signifies that thermal decomposition was only partial. No molecular structures of the compounds studied are known.

The quantum chemical calculations were performed with the Gaussian 09 program [5] and included full geometry optimization of neutral molecules at B3LYP/6-31G(2df,p) level. The vibrational analysis confirmed that the resulting geometry was the true minimum (no imaginary frequencies). Subsequently, the optimized DFT

* Corresponding author.

E-mail addresses: inovak@csu.edu.au (I. Novak), klasinc@irb.hr (L. Klasinc), sean.mcglynn@chemgate.chem.lsu.edu (S.P. McGlynn).



Scheme 1. Thioamides as electrophiles and nucleophiles (adapted from Ref. [1]). LA = Lewis acid, BB = Brønsted base, symbol R^2_2 indicates two R^2 functional groups.

Table 1

Vertical ionization energies: experimental (E_i /eV) and calculated (OVGF/eV) and orbital assignments (MO) in thioamides^{a-c}.

Compound	Band	E_i	OVGF	MO
1	X	(7.95)	7.75 (7.90)	n_S
	A	8.33	8.02 (8.11)	π_{SCN}
	B	(9.55)	10.12 (8.84)	n_O
2	X	7.80	7.69 (7.85)	n_S
	A	8.16	7.97 (8.06)	π_{SCN}
	B	(9.55)	10.09 (8.78)	n_O
3^b	X-A	8.01	7.72, 7.80 (7.46, 7.50)	π_b, π_{SCN}, n_S
	B	(8.55)	8.98 (8.22)	π_b
	C-D	9.24, 9.60	9.17, 10.23 (8.84, 9.56)	π_{SCN}, n_O
4	X	8.15	7.87 (7.57)	$\pi_b - n_N$
	A	(9.15)	8.84 (8.68)	π_b
	B	9.80	9.87 (8.76)	$n_{OCN} - n_O$
	C	10.71	10.55 (10.02)	π_{OCN}
Cyclohexanone	X	9.28	9.58	n_O
CH_3CSNH_2	X	8.35		n_S
	A	8.97		π_{SCN}
NH_2CHO	X	10.15		$n_N (\pi_{OCN})$
	A	10.4		n_{OCN}
$HCSNH_2$	X	8.70		n_S
	A	9.30		π_{SCN}

^a OVGF values and MO labels for bands <11 eV. OVGF values in brackets correspond to ionization energies of the second most stable tautomer B.

^b The sharp peaks at 10.16, 10.51 and 13.84 eV correspond to CS_2 , H_2S and CO_2 decomposition products, respectively. Peaks at 12.69 and 14.52 eV correspond to traces of water (moisture) in the sample, while peaks at 11.73 and 12.09 eV correspond to HBr calibrant.

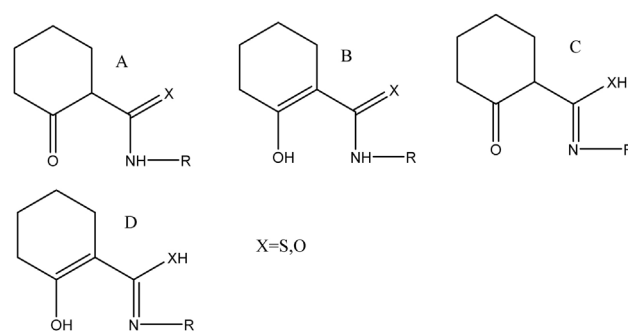
^c E_i values in brackets indicate adiabatic ionization energies.

Table 2

Difference in Gibbs free energies (kJ/mol) between (thio)amide tautomers A–D determined by high level composite ab initio G4MP2 method.

Compound	A	B	C	D
1	0.0	36.5	54.4	42.4
2	0.0	35.9	53.1	40.4
3	0.0	38.4	34.9	40.2
4	0.0	32.5	55.4	119.6

geometry was used as the input into the single point calculation using the outer-valence Green's function (OVGF) method and 6-311G(d,p) basis set [6]. This method obviates the need for using Koopmans approximation and provides vertical ionization energies with typical deviation of 0.3–0.5 eV (depending on the size of the basis set) from the experimental values. The total electronic energy for each molecule was computed using the high-level composite G4MP2 method [7] which has the root-mean-square deviation



Scheme 2. Structures of possible (thio)amide tautomers A–D.

of 4 kJ/mol. The method includes full geometry optimization at the B3LYP/6-31G(2df,p) level followed by the single point CCSD/6-31G(d) type calculations. The total electron energy was used to determine relative energies of possible tautomers. We have considered possible conformers obtained via rotation around single C–C bond between the cyclohexanone ring and (thio)amide group. There was no difference in the calculated ionization energies for different conformers, but there were noticeable differences between the sets of ionization energies for different tautomers e.g. the lowest energy tautomers A and B (Table 1).

3. Results and discussion

The HeI photoelectron spectra of the compounds studied are shown in Figs. 1–4. The spectral assignments are summarized in Table 1 and are based on OVGF calculations and comparison with the UPS of related molecules: cyclohexanone, CH_3CSNH_2 , $HCSNH_2$ and $HCONH_2$ [8–11]. The ionization energies of related molecules are included in Table 1.

3.1. Compounds 1 and 2

The photoelectron spectra are shown in Figs. 1–2 and the assignments are given in Table 1. The spectra in the ionization energy region below 11 eV, contain partially resolved bands (ionizations) corresponding to the total of three ionizations arising from sulphur lone pair (n_S), π -orbital localized on thioamide moiety (π_{SCN}) and the oxygen lone pair localized on cyclohexanone oxygen (n_O). n_S orbitals in **1** and **2** show considerable reduction in their ionization energies (by 0.75–0.9 eV) compared to $HCSNH_2$ or CH_3CSNH_2 . This decrease in ionization energy, is due to the inductive effect (destabilization) of alkyl substituents on the nitrogen atom. The reduction in ionization energy suggests that **1** and **2** are softer Lewis acids than the molecules $HCSNH_2$ or CH_3CSNH_2 . The ionization energy of the oxygen lone pair on the other hand is increased by only 0.27 eV compared to cyclohexanone. The similar trend of increasing ionization energy of n_O is observed in OVGF values. This observed energy increase together with the calculated OVGF energies and relative stabilities of different possible tautomers (Table 2) suggests that the dominant tautomers for **1** and **2** in the gas phase are keto–thio keto.

3.1.1. Compound 3

The HeI photoelectron spectrum is shown in Fig. 3 and its assignment is given in Table 1. The compound shows some decomposition upon heating in the gas phase as is evident from the presence of low intensity, sharp peaks which correspond to small molecules as products of decomposition. The sharp peaks include those relating to the small amounts of decomposition products, to water (moisture) or to HBr calibrant as indicated in Table 1. The ionization energies of orbitals localized on the thioamide group have similar

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