A Photoelectron Spectroscopic Study of Thioformamide

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The He I photoelectron spectrum of thioformamide ($HCSNH_2$) has been measured. On the basis of spectral features, CNDO/2 calculations, and sum rule considerations, the following assignments have been concluded. 1) Six ionization bands appearing below 17 eV correspond to six-p-type MOs and two bands in the region 17—20 eV correspond to s-type MOs. 2) The first ionization band is attributed to the highest occupied (in-plane) MO constructed mainly from the sulfur lone pair which is mixed to some extent with the σ_{CN} orbital. 3) The second and fourth bands are due to the out-of-plane MOs, mainly corresponding to the nitrogen lone pair and the π_{CS} orbital, respectively. 4) The remaining p-type bands may be interpreted in terms of σ_{CS}, σ_{CN}, and π_{NH_2} (pseudo pi) orbitals.

Photoelectron spectroscopy using a He 584 Å source provides valuable information on valence orbital structure as well as vibrational structure in ionized states.[1] The He I photoelectron spectra of simple amides and carboxylic acids were studied by Brundle *et al.*,[2] who payed a special attention to the assignment of the closely overlapped bands due to the n_O (oxygen nonbonding) and π_2 (antisymmetric pi) MOs. Only a few photoelectron works has been published on thiocarbonyl compounds. Kroto *et al.* [3-5] reported the photoelectron spectra of several pyrolytically produced unstable compounds, H_2CS, CH_3CHS, $(CH_3)_2CS$, and F_2CS. No photoelectron studies have so far been published on thioformamide, which is fairly stable in the gaseous phase at room temperature. Debies and Rabalais[6] have recently published the He I and II photoelectron spectra of some amino acids, urea and thiourea. Our primary concern in the present work is to study the valence orbitals of thioformamide by means of He I photoelectron spectroscopy.

Experimental

Measurements of He I photoelectron spectra were carried out with a high-resolution photoelectron spectrometer used previously.[7,8] Calibration of the ionization energy scale was carried out using known ionization energies of Xe as an internal standard. A gaseous sample was introduced through a vacuum glass line with a Teflon needle valve. No metal tube was used to avoid decomposition. The pressure in the spectrometer tank was 1×10^{-6} Torr before the photoelectron measurements and 1 to 5×10^{-5} Torr during the measurements. The ionization chamber of cylindrical type (14 mm in diameter and 27 mm long) was used. The electron analyzer of the spectrometer was operated at ±0.2 V.

The sample of thioformamide used was prepared by a reaction of formamide and phosphorus pentasulfide,[9] and purified by a recrystallization from cold ether and then from cold (>15 °C) ethylacetate. The infrared absorption spectrum of the sample was in a perfect agreement with what Suzuki[10] observed.

Results and Discussion

The He I photoelectron spectrum of thioformamide below 20 eV is shown in Fig. 1, from which the following spectral features may be seen. 1) The first two ionization bands are well resolved with vibrational structure in the region 8.5—10 eV. 2) The third and fourth bands are considerably overlapped with each other in the region 12.5—13.5 eV, the latter being much sharper. 3) The fifth band appearing at about 14.1 eV is much weaker and the sixth band at 15.0—16.5 eV consists of three sub-bands associated with vibrational structure. 4) There are two more additional weak bands in the region 17—20 eV. The individual ionization bands in the photoelectron spectrum in Fig. 1 are indicated by vertical lines with the numbering.

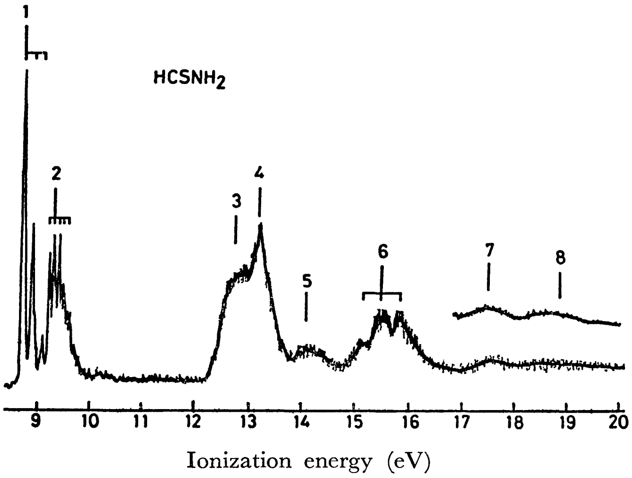

Fig. 1. He I photoelectron spectrum of thioformamide.

All the vertical ionization energies obtained from the thioformamide spectrum are summarized in Table 1.

Table 1. Vertical ionization energies (eV) and orbital assignments of thioformamide

	Vertical ionization energy	Orbital assignment Sym. (Main character)
I_1	8.70	$a'(n_S)$
I_2	9.30	$a''(n_N)—\pi_2$
I_3	12.80	$a'(\sigma_{C=S})$
I_4	13.18	$a''(\pi_{C=S})—\pi_1$
I_5	14.1_5	$a'(\pi_{NH_2})$
I_6	15.52	$a'(\sigma_{CN})$
I_7	17.7_0	$a'(s_S)$
I_8	18.9_0	$a'(s_C)$

As previously done,[7,8,11,12] we use the following p-type localized molecular orbitals (LOs) in order to represent main orbital features of the p-type bands: n_S (sulfur nonbonding), n_N (nitrogen nonbonding), π_{CS} (C=S pi bonding) σ_{CS} (C=S sigma bonding), σ_{CN} (C–N sigma bonding), and π_{NH_2} (amino-group pseudo pi). Since thioformamide has a planar molecular structure (C_s),[13] bonding and antibonding pi MOs (designated as π_1 and π_2, respectively) may be formed from the out-of-plane n_N and π_{CS} LOs. The valence orbitals of thioformamide therefore may be explained in terms of the two out-of-plane p-type LOs (n_N and π_{CS}), four in-plane p-type LOs (n_S, σ_{CS}, π_{NH_2}, and σ_{CN}) and three in-plane s-type LOs (s_C, s_S, and s_N).

In most of the saturated and unsaturated aliphatic compounds so far studied,[7,8,11,12] all p-type photoelectron bands are observed below about 18 eV. From the numbers of p- and s-type LOs, it may be reasonably considered that the six bands appearing below about 17 eV are due to the p-type LOs and the remaining two bands are due to the s-type LOs.

The third, nitrogen s-type band of thioformamide is expected to appear around 27 eV (beyond the He I region), since Potts *et al.*[14] have reported that the nitrogen s-type band of the methylamine is located at 27.5 eV. The carbon s-type bands of the C=O groups in H_2CO and CH_3CHO appear around 18—19 eV.[7] No sulfur s-type bands have so far been reported.

In the present work, we carried out CNDO/2 calculations[15] of orbital energies using a recently available geometry[13] and obtained the following orbital assignments under Koopmans' theorem:[16] $I_1 \rightarrow \varepsilon_1(a', n_S)$, $I_2 \rightarrow \varepsilon_2(a'', \pi_2)$, $I_3 \rightarrow \varepsilon_3(a', \sigma_{CS})$, $I_4 \rightarrow \varepsilon_4(a', \pi_{NH_2})$, $I_5 \rightarrow \varepsilon_5(a'', \pi_1)$, $I_6 \rightarrow \varepsilon_6(a', \sigma_{CN})$, $I_7 \rightarrow \varepsilon_7(a', s_S)$, $I_8 \rightarrow \varepsilon_8(a', s_C)$, and $I_9 \rightarrow \varepsilon_9(a', s_N)$. However, this assignment of I_4 to the π_{NH_2} seems to be incorrect, since the ionization of an electron from the pseudo π orbital always gives rise to a broad band as in methylamine. From the spectral shape, therefore, the fourth, sharp band may be assigned to the out-of-plane π_1 rather than the in-plane π_{NH_2} LO. This may also be supported by the sum rule consideration mentioned later.

The sum rule previously proposed[7,8,11,12] may approximately hold for the vertical ionization energies associated with the out-of-plane LOs of thioformamide, as summarized in Table 2. In the sum rule consideration, we used the empirical ionization energies given in Table 3 which are based on the experimental vertical ionization energies of simple molecules (I^0). The I^0 values given for the n_N and $\pi_{C=S}$ LOs in Table 3 were taken from the available photoelectron data of the first ionization energy of ammonia and the second ionization energy of thioformaldehyde, respectively. As shown in Table 2, good agreement is obtained between the experimental and calculated partial sums for thioformamide. A similar sum rule consideration is also demonstrated for formamide in Table 2, a considerably good agreement being again obtained between experiment and calculation. The orbital assignments finally concluded in the present work (Table 1) therefore differ from those of the CNDO/2 calculations in the order of the fourth and fifth inner orbitals.

Table 2. Experimental and calculated partial sums, $P(a'')$, for the out-of-plane LOs

Compound	$(I_i s) \rightarrow$ (LOs)	$-P(a'')$, eV Expt.	 Calcd.
$HCSNH_2$	$(I_2, I_4) \rightarrow a''(n_N, \pi_{C=S})$	22.48	22.66
$HCONH_2$	$(I_2, I_4)^{a)} \rightarrow a''(n_N, \pi_{C=O})$	25.27	25.38

a) $I_2 = 10.52$ eV, $I_4 = 14.75$ eV, taken from Ref. 2.

Table 3. Empirical energies (I^0, eV) used for the localized molecular orbitals (LOs) in the sum rule considerations

$I^0(n_N) = 10.88^{a)}$
$I^0(\pi_{C=S}) = 11.78^{b)}$
$I^0(\pi_{C=O}) = 14.50^{c)}$

a) I_1 of NH_3; A. W. Potts and W. C. Price, *Proc. Roy. Soc., Ser. A*, **326**, 181 (1972). b) I_2 of H_2CS; Ref. 4. c) I_2 of H_2CO; C. R. Brundle, M. B. Robin, N. A. Kuebler, and H. Basch, *J. Am. Chem. Soc.*, **94**, 1451 (1972).

The vibrational structures of the first and second bands are shown in an expanded scale in Fig. 2. The vibrational intervals of about 1460 cm⁻¹ which appear in the first band of $HCSNH_2$ are probably due to the C–N stretching (about 1450 cm⁻¹ in the ground state of neutral liquid thioformamide). The second band of $HCSNH_2$ shows the vibrational intervals of about 730 cm⁻¹ which are probably assigned to the C–S stretching (about 840 cm⁻¹ in the ground state of neutral liquid thioformamide). These vibrational progressions seem to be closely associated with the facts that the orbital interactions exist between the n_S and σ_{CN} LOs in the highest occupied MO and between the n_N and π_{CS} LOs in the second inner MO.

The experimental orbital levels of thioformamide based on Koopmans' theorem are shown in Fig. 3, compared with those of its some related compounds. The LO levels (n_N, π_{CS}, and π_{CH_3}) are also shown in

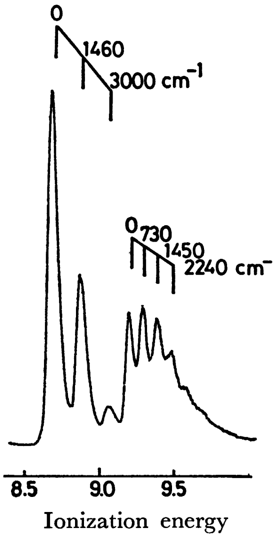

Fig. 2. The vibrational structure of the first two ionization bands of $HCSNH_2$ shown in an expanded scale.

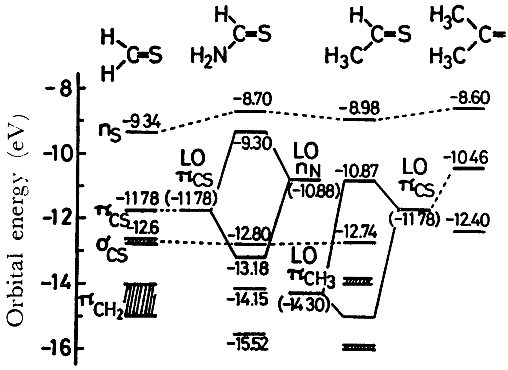

Fig. 3. Experimental (Koopmans' theorem) orbital correlation diagrams for thioformamide and its related compounds. The LO levels are based on the photoelectron data of simple compounds. Orbital energies for H_2CS, CH_3CHS, and $(CH_3)_2CS$ were taken from the literatures.[3,4] (The -12.6 eV level of H_2CS was tentatively assumed from the sharp peak of the available photoelectron spectrum.)

Fig. 3, together with their energy values in parentheses. The interaction schemes of the out-of-plane LOs are indicated by connecting the levels with solid lines. The σ_{CS} level of thioformamide is located at -12.80 eV, close to those of thioformaldehyde and thioacetaldehyde (-12.6 and -12.7 eV, respectively).

The assignment of the first band to the n_S rather than the n_N LO was also confirmed without Koopmans' theorem in the present CNDO/2 calculations by obtaining the difference in total energy between thioformamide and its cation in the ground state, a calculated ionization energy of 9.43 eV being obtained.

According to an electronic absorption study by Hosoya *et al.*,[17] the ultraviolet absorption bands of thioformamide in the regions 260—280 and 220—240 nm may be attributed to electron transitions to the $\pi^*_{C=S}$ orbital from the sulfur and nitrogen lone pair orbitals, respectively. The difference in transition energy between these absorption bands is 0.8 eV. It is interesting to note that this transition-energy difference of thioformamide is considerably close to the separation of the first two photoelectron bands (0.6 eV).

References

1) D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, "Molecular Photoelectron Spectroscopy," Wiley, New York (1969).

2) C. R. Brundle, D. W. Turner, M. B. Robin, and H. Basch, *Chem. Phys. Lett.*, **3**, 292 (1969).

3) H. W. Kroto and R. J. Suffolk, *Chem. Phys. Lett.*, **15**, 545 (1972).

4) H. W. Kroto, B. M. Landsberg, R. J. Suffolk, and A. Vodden, *Chem. Phys. Lett.*, **29**, 265 (1974).

5) H. W. Kroto and R. J. Suffolk, *Chem. Phys. Lett.*, **17**, 213 (1972).

6) T. P. Debies and J. W. Rabalais, *J. Electron Spectrosc.*, **3**, 315 (1974).

7) K. Kimura, S. Katsumata, T. Yamazaki, and H. Wakabayashi, *J. Electron Spectrosc.*, **6**, 41 (1975).

8) S. Katsumata and K. Kimura, *J. Electron Spectrosc.*, **6**, 309 (1975).

9) R. Willstater and T. Werth, *Ber. Deut. Chem. Ges.*, **42**, 1908 (1909).

10) I. Suzuki, *Bull. Chem. Soc. Jpn.*, **35**, 1286 (1962).

11) K. Kimura, S. Katsumata, Y. Achiba, H. Matsumoto, and S. Nagakura, *Bull. Chem. Soc. Jpn.*, **46**, 373 (1973).

12) T. Yamazaki and K. Kimura, *Bull. Chem. Soc. Jpn.*, **48**, 1602 (1975).

13) R. Sugisaki, T. Tanaka, and E. Hirota, *J. Mol. Spectrosc.*, **49**, 241 (1974).

14) A. W. Potts, T. A. Williams, and W. C. Price, *Discuss. Faraday Soc.*, **54**, 104 (1972).

15) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGrad-Hill, New York (1970). The present CNDO/2 calculations were carried out with a library program written by H. Itoh, K. Yoshida, and T. Nakamura of Hokkaido University.

16) T. Koopmans, *Physica*, **1**, 104 (1934).

17) H. Hosoya, J. Tanaka, and S. Nagakura, *Bull. Chem. Soc. Jpn.*, **33**, 850 (1960).