

The Electronic Structure of Propyl 3-Mercaptocrotonate Studied by Photoelectron Spectroscopy*

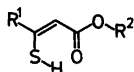
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Extending our photoelectron (PE) spectroscopic studies on β -thioxo carbonyl compounds² we have studied for comparative reasons the electronic structure of a representative β -thioxo ester. Contrary to the β -thioxoketones, which exist as rapidly interconverting enol-enethiol tautomers,³ the β -thioxo esters exist practically exclusively in the enethiol form **1**.⁴ We have recorded the PE spectrum of propyl 3-mercaptoprotonate **1a** and performed MNDO molecular orbital calculations on methyl 3-mercaptoprotonate **1b**. Experiment as well as theory indicate the ordering of the four lowest ionization energies to be $\pi_4 \ll n_O < \pi_3 \sim \pi_2$.



1a: R¹ = CH₃, R² = C₃H₇

1b: R¹ = H, R² = CH₃

* β -Thioxo esters **4**: For part **3** see Ref. 1.

The PE spectrum of **1a** contains three bands below the σ onset at 8.81, 10.05 and 10.96 eV, the latter exhibiting a shoulder at 10.58 eV (Fig. 1). The shape of the first band suggests the presence of vibrational fine structure, but attempts to get it properly resolved were unsuccessful. We assign the peak at 8.81 eV to ionization from the π_4 orbital (Fig. 2), possessing mainly S_{3p} lone pair character. The destabilization of the π_4 orbital relative to the S_{3p} orbital of methanethiol⁵ (Fig. 2) arises from interaction of the sulfur lone pair with the π system and from the extension of the molecular framework.⁶ The PE spectrum of ethyl (*E*)-crotonate **3** exhibits two low energy ionizations at 10.11 eV and 10.71 eV, where the former value corresponds to the n_O orbital in the plane of the molecule and the π_{CC} orbital, and the latter to the π_2 orbital (the anti-bonding combination of the O_{2p} lone pairs in the ester group).⁷ Since the areas of the peaks of **1a** suggest that the band with maximum at 10.96 eV and its shoulder at 10.58 eV correspond to two ionizations, we locate three ionizations between 10 and 11 eV. The n_O orbital (10.11 eV in **3**) placed in the nodal plane of the π -type orbitals must be expected to be only slightly affected by the structural changes **3** \rightarrow **1a**, indicating that the peak at 10.05 eV without doubt corresponds to the n_O orbital. On the other hand, the π_{CC} orbital (10.11 eV in **3**) should interact strongly with the S_{3p} lone pair. Accordingly, the bonding combination will be stabilized. This stabilization must be expected to be larger than the stabilization of the π_2 orbital (10.71 eV in **3**) because of the remote character of the S_{3p} orbital relative to the π_2 orbital. An opposite effect on the π_2 orbital due to extension of the alkyl group (**3**: -OEt \rightarrow **1a**: -OPr) will tend to destabilize the orbital by 0.1–0.2 eV.⁸ This leads us to the correlation shown in Fig. 2.

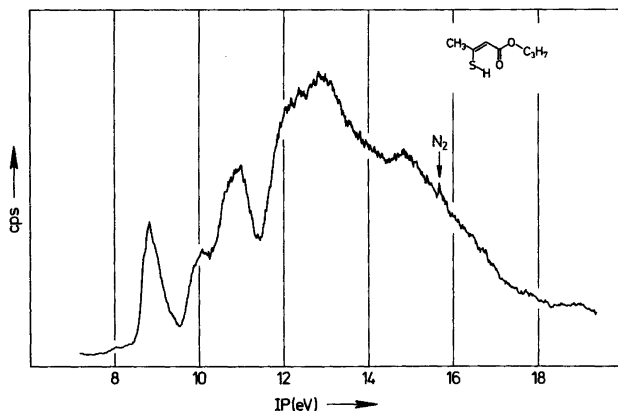


Fig. 1. Photoelectron spectrum of propyl 3-mercaptoprotonate **1a**.

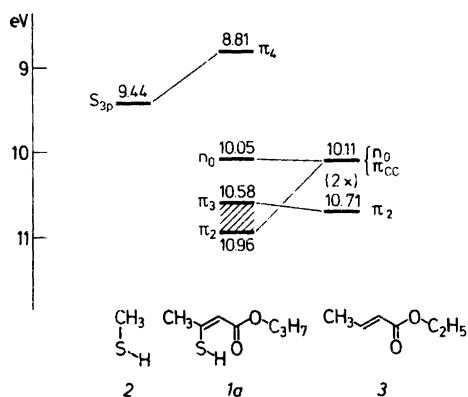


Fig. 2. Energy level correlation diagram. The numerical values refer to experimentally determined PES ionization energies (eV).

To support our interpretation of the above PE spectrum we have performed an MNDO molecular orbital calculation of methyl 3-mercaptoacrylate *1b*, the simplest enethiolized β -thio ester. The orbital energies and densities of the MNDO⁹ geometry optimized structure of the compound is shown in Fig. 3. The highest occupied molecular orbital (HOMO) of the molecule, placed well above the three following orbitals, is the anti-bonding combination of the S_{3p} lone pair and the π_{CC} orbital (π_4).

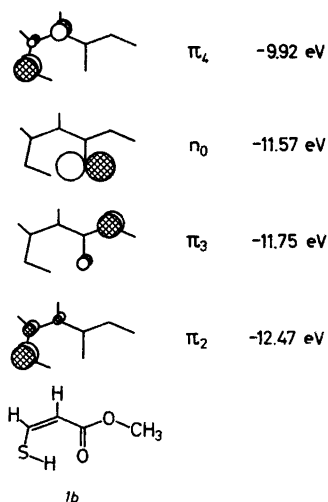


Fig. 3. MNDO calculated orbital energies (eV) and densities. The circle diameters are proportional to the square of the contributing atomic orbital coefficients.

Both the PE spectroscopy and the MNDO calculations indicate that the order of the lowest ionization energies are $\pi_4 \ll n_0 < \pi_3 \sim \pi_2$, where π_4 corresponds to $n_s - \pi_{CC}$, π_3 corresponds to the anti-bonding combination of the oxygen lone pairs (the π_2 orbital in esters), and π_2 to $n_s + \pi_{CC}$. The above findings thus disclose a clear relationship between the electronic structures of enethiol tautomeric forms derived from β -thioxoketones² and β -thio esters, respectively.

Propyl 3-mercaptocrotonate *1a* was selected arbitrarily for this study as a single, typical representative of the group of normally enethiolized β -thio esters, since earlier ¹H NMR and UV-VIS spectroscopic studies⁴ of these have demonstrated very close similarities as regards both their geometric and their electronic structures.

Experimental. The synthesis of *1a* has been described previously.⁴ Purity was checked by ¹H NMR spectroscopy before recording the PE spectra. The PE spectra were recorded on a PS-18 spectrometer (Perkin-Elmer) with an He(I) source and calibrated with a mixture of argon and xenon introduced into the target chamber simultaneously with the sample. The spectra were recorded at room temperature. The experimental resolution was 30 meV. The reported ionization energies are averages of four determinations.

1. Duus, F. *J. Chem. Soc. Perkin Trans. 1*, 292 (1978).
2. Jørgensen, F. S., Carlsen, L. and Duus, F. *J. Am. Chem. Soc. In press*.
3. Duus, F. and Anthonen, J. W. *Acta Chem. Scand. B* 31 (1977) 40; Duus, F. *J. Org. Chem.* 42 (1977) 3123; Carlsen, L. and Duus, F. *J. Am. Chem. Soc.* 100 (1978) 281; Carlsen, L. and Duus, F. *J. Chem. Soc. Perkin Trans. 2* (1979) 1532.
4. Duus, F. *Tetrahedron* 28 (1972) 5923.
5. Bock, H. and Wagner, G. *Angew. Chem.* 84 (1972) 119.
6. Lewitt, L. S. and Levitt, B. W. *J. Org. Chem.* 37 (1972) 332.
7. Sustmann, R. and Trill, H. *Tetrahedron Lett.* (1972) 4271.
8. Sweigart, D. A. and Turner, D. W. *J. Am. Chem. Soc.* 94 (1972) 5592.
9. Dewar, M. J. S. and Thiel, W. *J. Am. Chem. Soc.* 99 (1977) 4899, 4907; Dewar, M. J. S., McKee, M. L. and Rzepa, H. S. *Ibid.* 100 (1978) 3607.

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