X-Ray Photoelectron Spectroscopic Study of Captodative Olefins: Electronic Structure of α-Thio-acrylonitrile Derivatives

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The atomic charge distribution in various captodative olefins has been determined by *X*-ray photoelectron spectroscopy. The experimental data reflect the reactivity trend observed in radical addition.

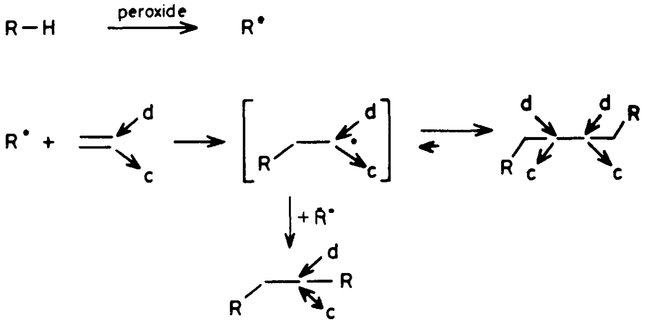
Recently[1] we introduced the concept of radicophilicity. According to this concept, electrophilic or nucleophilic radicals add to captodative (cd) olefins carrying a donor group (d) and an acceptor group (c) on the same carbon atom, thereby producing stabilised radical intermediates. This stabilisation is sufficent to suppress polymerisation in favour of formation of adduct-dimers or more rarely of double adducts. These reactions have been applied to the synthesis of various compounds,[2,3] and the polarity of captodative olefins has been investigated by various physicochemical techniques.[4]

As part of these investigations, we report here the results of an *X*-ray photoelectron spectroscopic (XPS) study on a series of captodative olefins (Table) having a nitrile group as acceptor and an alkylthio [MeS (**1**) or Bu^{t}S (**2**)] or phenylthio group (**3**) as donor. All are very efficient traps for nucleophilic methyl radicals, but slightly less for electrophilic t-butoxyl radicals.[2,3] For comparison, the work was extended to include two other olefins, the α-phenylthiostyrene (**4**), which traps in very good yield the t-butoxyl radical; and the 2,3-bis(methylthio)-maleonitrile (**5**), in order to investigate the charge delocalization in an olefin exhibiting both cross-conjugation and push–pull conjugation through the double bond.

Experimental

Sample Synthesis.—The olefins were synthesized as described in the literature: ref. 5 for compounds (**1**)—(**3**); ref. 6 for (**4**) and ref. 7 for (**5**).

Instrumentation and Data Handling.—*X*-Ray photoelectron spectra were recorded with an HP 5950 A spectrometer, using monochromatized Al-$K_{\alpha 1,2}$ radiation ($h\nu$ 1 486.6 eV). Powdered samples [(**4**), (**5**)] were pressed into pellets and deposited on a gold-plated substrate. Liquid samples [(**1**)—(**3**)] were vaporised in the sample-handling chamber of the spectrometer by means of a needle valve, and condensed as thin films onto a gold plate, precooled with liquid nitrogen. During analysis, the samples were kept at low temperature to maintain the high vacuum required in the spectrometer ($\leqslant 2 \times 10^{-9}$ Torr). An electron flood gun was used to neutralize the surface-charging effect created by the ejection of the photoelectrons. The spectra were calibrated by reference to an internal standard: the C1*s* peak of benzene and aliphatic groups was set at 284.5 eV.[8,9] Peak positions and areas were obtained by a weighted least-squares fitting of model curves (50% Gaussian, 50% Lorentzian) to the experimental data, using the Simplex method minimizing the χ square.[10] The reproducibility of the various measurements was very good and yielded reliable experimental binding energies (within 0.1 eV).



Results and Discussion

The binding energies of C1*s*, N1*s*, and S2$p_{3/2}$ core levels, and S3*p* lone pairs, are listed in the Table.

Carbon.—The C1*s* peaks of compounds (**1**)—(**3**) and (**5**) are shown in Figure 1. The positions and the relative intensities of the various components are given in the Table.

Fujikawa *et al.*[11] have reported theoretical and experimental results on various molecules containing the C≡N group. The net charges on the carbon atoms in acrylonitrile (CH_2=CH–C≡N), as obtained from CNDO/2 calculations, are respectively +0.092 for C≡N, +0.010 for CH, and −0.022 for CH_2. The gas-phase XPS binding energies are well explained by introducing these charge densities in the classical electrostatic-potential model.[12]

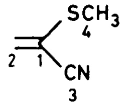
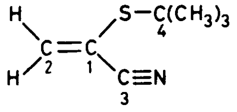
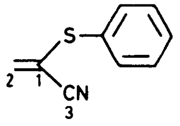
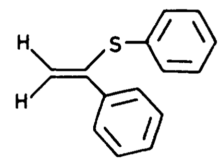
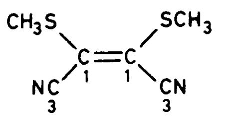
From these observations, we attribute, for compounds (**1**)—(**3**), the high binding-energy component (E_B = 286.4 ± 0.1 eV) to C-1 and C-3. In compound (**5**), these atoms have a less positive charge (E_B = 285.6 and 285.8 eV).

The C1*s* line of (**4**) shows no peculiar features: the fourteen carbon atoms of the molecule have nearly the same charge density.

Heteroatoms.—For compounds (**2**) and (**3**), the N1*s* core level binding energy is 399.6 eV, indicating a negative charge on the nitrogen atoms.[11,13] In the case of (**1**) and (**5**), this negative charge is smaller. The S2$p_{3/2}$ binding energies in compounds (**2**), (**3**), and (**5**) are similar to the values observed with aliphatic and benzylic sulphides or disulphides,[14,15] and reveal a weak negative charge on the chalcogen. For the other two molecules (**1**) and (**4**), we find the same S2*p* binding energy as in diphenyl sulphide and disulphide,[14,15] in which the charge on sulphur is negligible.

It has been shown in detail[15] that the intensity and position

Table. Binding energies (eV) of core levels and S3*p* lone pairs of various α-thio-acrylonitrile derivatives and α-phenylthiostyrene

	Compound	C1*s*			N1*s*	S2*p*	S3*p*
(1)		286.4 C-1, C-3	285.2 C-2	284.5 C-4	399.3	163.7	3.5
(2)		286.4 C-1, C-3	285.2 C-2, C-4	284.5 CH_3	399.6	163.9	3.6
(3)		286.3 C-1, C-3	284.9 C-2	284.5 Phenyl	398.6	164.3	3.1
(4)			284.5			164.1	3.0
(5)		285.8 C-3 (or C-1)	285.6 C-1 (or C-3)	284.5 CH_3	398.2	163.5	2.7

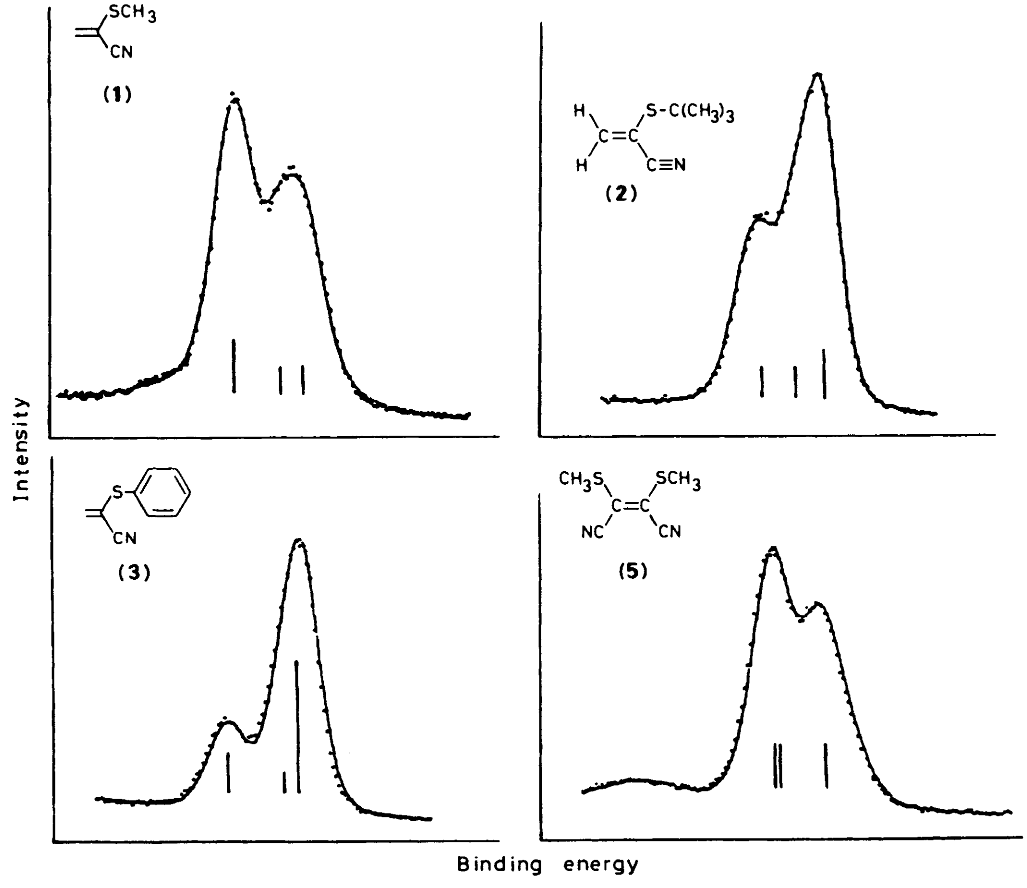


Figure 1. XPS C1*s* spectra of compounds (**1**)—(**3**), and (**5**) (dotted lines, experimental data; unbroken lines, simulated spectra); positions and relative intensities of the various components are indicated by the vertical lines; binding-energy values are listed in the Table

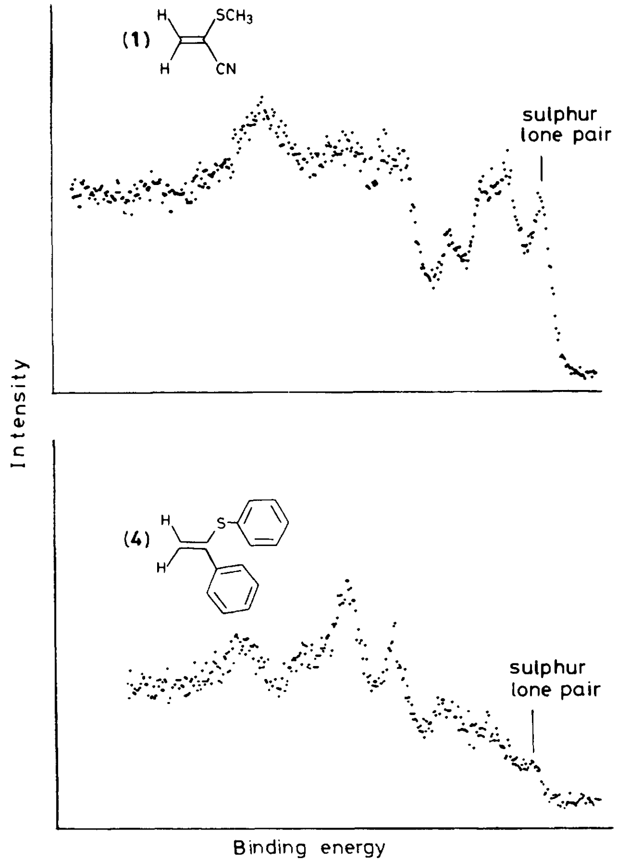


Figure 2. XPS valence band spectra of compounds (**1**) and (**4**); binding energies of the S3*p* lone-pair levels are given in the Table.

of the XPS peak related to the ionization of the sulphur lone pair molecular orbital provides a powerful means of estimating the interaction between the chalcogen and the carbon skeleton (S2*p*–C2*p* interaction). The intense S3*p* peak observed for compounds (**1**), (**2**), and (**5**) (Figure 2) clearly corresponds to a lone pair strongly localized on the sulphur atom. Its shift to low binding energy is similar to that reported for the S2*p* core levels. On the other hand, in compounds (**3**) and (**4**), the weak S3*p* signal reflects a strong interaction between the lone pair and the ethylenic or benzenic framework.

Chemical Reactivity.—The charge distribution of the captodative olefins is well described by the XPS results. In particular, the C-2 atomic charge appears to decrease in the sequence (**1**) ~ (**2**) > (**3**) > (**4**) (see Table). This implies that the charge on the photoionized atom predominantly influences the chemical shift, a direct relationship is therefore expected between the electron binding-energy shifts and the atomic charges. With carbon compounds, good linear correlations have been obtained for large series of compounds.[12] From these relations, the positive charge on C-2 atom is estimated to be +0.10 in compounds (**1**) and (**2**) and +0.05 in compound (**5**). It would be zero in compound (**4**).

These differences can be directly related to the efficiency for the trapping of an electrophilic radical such as t-butoxyl. Indeed, experiments have shown the reactivity sequence (**4**) $\gg$ (**2**) ~ (**1**).[3] It was not possible to achieve any preparative t-butoxyl addition with olefins (**3**) and (**5**). From XPS predictions, the t-butoxyl radical reactivity towards compound (**3**) should be intermediate between those observed for (**2**) and (**1**).

This parallel between the atomic charges and the reactivity sequence underlines the role played by polar effects in the addition of the t-butoxyl radical to various captodative olefins and α-phenylthiostyrene. Furthermore, the observed reactivity pattern agrees with various theories affirming that radical addition[16] to unsaturated systems is mainly governed by steric and polar effects.

Acknowledgements

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