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ESCA MEASUREMENTS ON IRON TRICARBONYL COMPLEXES OF SOME ORGANOSULFUR COMPOUNDS

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Summary

The ESCA spectra of some iron tricarbonyl complexes of thiophene and dihydrothiophene derivatives are reported, assigned, and interpreted in the light of simple bonding theories. This is the first account of the ionization potentials of the various atoms in iron tricarbonyl complexes.

Introduction

ESCA (Electron Spectroscopy for Chemical Analysis) has proved its potential as a tool for obtaining new insights into structural and bonding problems in organic [1] and organometallic [2] chemistry. Notable applications have been made in correlating charges in atoms [3], in investigations of the polarity of chemical bonds [4], in elucidating structural problems (a good example being the assignment of the structure of doubly oxidized cystine [5]) and, of special importance to this work, in determining the mode of bonding of sulfoxides as ambident ligands to metals [6].

We present here the ESCA spectra of a series of iron tricarbonyl complexes of some thiophene and dihydrothiophene derivatives. We find that the spectra provide new insights into the physicochemical properties of these compounds.

Results and discussion

The relevant spectral data for the organometallic compounds are presented in Table 1 together with data for some noncomplexed organosulfur compounds included for comparison purposes.

Nordling et al. [4,11] observed that for carbon compounds in general the C1s

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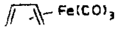
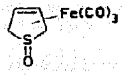
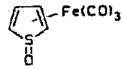
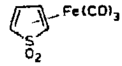
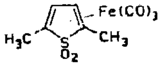
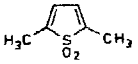
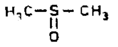
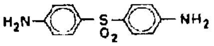
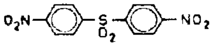
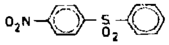
TABLE 1

IONIZATION POTENTIALS IN eV

		$C1s(sp^2+sp^3)$	$C1s(CO)$	$S2p_{3/2}$	$O1s(SO/SO_2)$	$O1s(CO)$	$Fe2p_{3/2}$ [a]
	I [b]	285.0	287.4			533.5	709.1
	II [c]	285.5(br)	287.3	167.0	532.0	533.5	709.1
	III [d]	284.7	287.4	165.8	530.6	533.5	709.1
	IV [e]	284.7	287.3	167.5	531.5	533.6	709.1
	V [e]	285.0	287.4	167.6	531.4	533.4	709.1
		285.0		167.9	531.6		
	f			164.5			
	f			166.5	532.4		
	f			166.7	531.7		
	f			168.1	532.1		
	f			167.9	532.3		
	f			167.8	532.3		

[a] The $Fe2p_{3/2}$ ionization potential is used as a reference to correlate the spectra of II—V. [b] See ref. 7. [c] See ref. 8. [d] See ref. 9. [e] See ref. 10. [f] ESCA values published in the literature [4] with the sp^3C, CH_3 value of 285.0 eV as calibration.

electrons from solid samples appear as sharp peaks with 1.6 eV as a typical value for the width at half maximum intensity in the ESCA measurement. The normal value for the sp^3C, CH_3 segment is 285.0 eV, which was used as a calibration point for assigning this absorption in V. All the carbons of the ligand in V appear as a slightly broadened (1.8 eV) C1*s* absorption but distinction between the sp^3 and sp^2 carbon atoms was not possible.

On the basis of this calibration the $Fe2p_{3/2}$ line in V is found to be at 709.1 eV; to enable further calibration the $Fe2p_{3/2}$ lines for complexes I—IV were also assigned this value.

Assignment of the remaining C1*s* absorptions of the simplest complex (I) was based on the intensities of the olefinic relative to the carbonyl absorptions. It was clear that the peak at 287.4 eV corresponds to the C1*s* absorption of the latter. The only remaining absorption is at 533.5 eV and this must obviously be assigned to the O1*s* absorption. Continuation of such reasoning allowed the

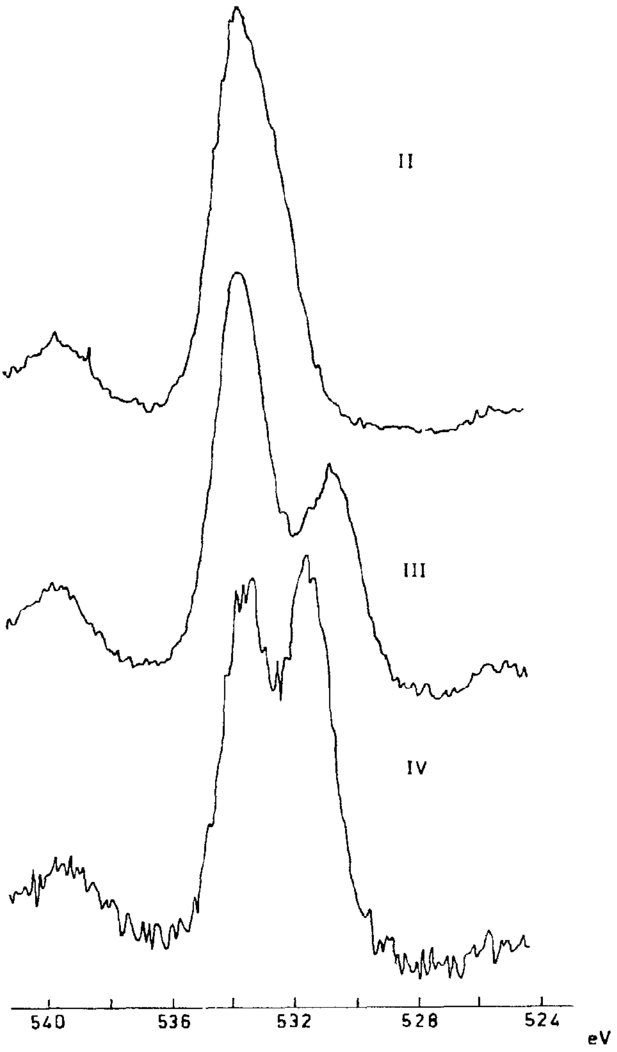


Fig. 1. The ESCA spectra of the O1*s* ionization potentials of the compounds II, III and IV.

assignment of all the absorptions for complexes II—V. Some representative spectra are shown in Fig. 1.

The strong degree of bonding of the carbonyl C to the metal and the relatively high positive charge on the carbonyl oxygen suggested by the high ionization potentials are consistent with the resonance $^{-}$Fe—C≡O^{+} ↔ Fe=C=O. An especially relevant observation revealed from inspection of the peak positions for the carbonyl atoms is that in the complexes I—V the iron tricarbonyl segment has similar properties in all the complexes. This suggests that the iron carbonyl portion may be used as a general reference in π- as well as σ-bonded iron tricarbonyl complexes.

Complex II is of interest in that the sulfoxide is a potentially ambident ligand, so that the iron might bond to either oxygen or sulfur. Su and Faller [6], on the

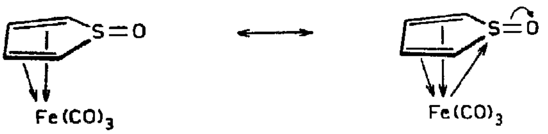


Fig. 2.

basis of measurements of a large number of Ni, Co, Mn, Zn, Cu, etc. chloride complexes with dimethyl, dibenzyl and diphenyl sulfoxides, have postulated that the difference between the $S2p_{3/2}$ and O1*s* ionization potentials of the complexed sulfoxide will reveal the type of bonding (for the background to this approximation see ref. 6). For metal—S bonding this difference was found to be 365.0 (±0.3) eV, whereas for metal—O bonding it is 365.8 (±0.3) eV. For complex II, this shift amounts to 365.0 eV, indicating, according to the Su and Faller criterion, that the metal is bonded to S rather than O. This conclusion is erroneous. The crystal structure of II has been reported [8,12], and reveals that iron is bonded to the oxygen of the sulfoxide. We conclude that the Su and Faller criteria cannot be extrapolated to iron tricarbonyl complexes of sulfoxides.

For complex III [9], the ionization potentials of the $S2p_{3/2}$ as well as the O1*s* of the sulfoxide are unusually low relative to complex II or to the average values for uncomplexed sulfoxides [4]. A simple qualitative explanation is found in the backbonding interaction indicated in the mesomeric structures, that in III the sulfur (which is electropositive relative to oxygen) can by back-donation take up directly or via the ring an electron pair from the iron carbonyl moiety to form an "aromatic" ring system (see Fig. 2). Comparison of various $S2p_{3/2}$ binding energies reveals that the S atom in III is much more electronegative than a normal sulfoxide and resembles more closely the sulfur of thiophene. This explanation of the ESCA behaviour of III bears a close analogy to the explanation of IR spectra, dipole moments, and chemical reactivity of fulvene [13] and cyclopentadienone [14] complexes (see Fig. 3). The large shifts of the ionization potentials found for both the oxygen and the sulfur atoms of the sulfoxide in III indicate that there are relatively more (about 0.6

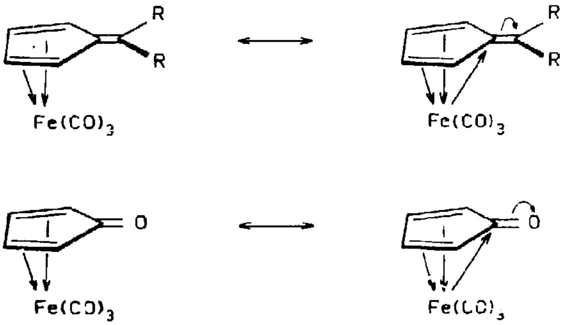


Fig. 3.

[15]) electrons on these atoms (hence a more ionic character of the bond) in III than in II, for example.

If such back-donation occurs this will affect the Fe atom and therefore the Fe2$p_{3/2}$ ionization potential. This effect will not be seen, however, since we have used the Fe2$p_{3/2}$ line as a reference to correct for charge effects. That the C1s and O1s absorptions of the carbonyls also do not change relative to Fe indicates that back-donation must occur from an orbital delocalized over the entire iron carbonyl moiety.

If this suggestion of back-donation in III is valid then we must accept that such an effect plays at best only a minor role in the thiophene-sulfone complexes IV and V, and this is consistent with the experimental results. It is attractive to postulate that the ligands in this case are incapable of obtaining any "aromaticity" because of the unavailability of the necessary sextet of electrons. However, refined theoretical calculations would be required to confirm * or refute this suggestion.

Experimental

The experiments were performed using an AEI ES 200 spectrometer with a PDP 8 data handling facility. The sample chamber of the spectrometer was modified to accept a liquid nitrogen cooled cryopump of a capacity such that the vacuum in the vicinity of the sample is even better than the measured vacuum, which was in most cases 10^{-9} Torr during a measurement. The cryopump also allowed working with cooled samples without serious problems from either water or hydrocarbon build-up on the surface. All samples were sublimed onto a cooled sample holder (—100°C) in the sample chamber of the spectrometer, using either the AEI sample holder for materials of low volatility or the holder for volatile materials. During sublimation the pressure rose to about 2—3×10^{-8} Torr. All charging-up effects were corrected by taking the Fe2$p_{3/2}$ binding energy as a reference as described.

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* Recent calculations [16] reveal that thiophene *S,S*-dioxide indeed has more dienic character than thiophene *S*-oxide.

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