

and shifted into the red by approximately 5000 cm^{-1} compared with the corresponding transitions of $\text{Cr}(\text{CO})_6$.⁸

The isolation of either metal atoms or metal complexes in the V/N₂ and Cr/N₂ cocondensation reactions implies that a very delicate balance between the activation energy for complexation and the thermal energy available at the reaction zone must exist, the latter being intimately related to the temperature at which the deposition is conducted. The fact that the corresponding V/CO and Cr/CO reactions proceed to completion even at 6 K means that complex formation for the carbonyls compared with the respective dinitrogen complexes is a more facile process. Whether this is because of a lower energy of activation or a higher heat of reaction for the carbonyls in the reaction zone, or both, cannot be ascertained. What is clear, however, is the subtle temperature dependence of product yield, an extremely important factor to take into account when performing direct syntheses with metal atoms.

Acknowledgments. We wish to thank the National Research Council of Canada and the Atkinson Foundation for financial support. T.A.F. thanks the South African Council for Scientific and Industrial Research for financial support.

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π -Donor Relaxation in the Oxygen 1s Ionization of Carbonyl Compounds

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Abstract: Oxygen 1s and carbon 1s binding energies have been measured for a wide variety of compounds containing the carbonyl group. It is concluded that most of the oxygen 1s ionizations include a rather large amount of electronic relaxation corresponding to π electron donation from the groups bonded to the carbonyl groups. The data are analyzed in two different ways to derive π -donor relaxation energies. The two resulting sets of relaxation energies are in fair agreement, and either set may be used to estimate the relative π -donor abilities of substituents.

The oxygen 1s binding energies of compounds containing the keto group, $>\text{C}=\text{O}$, do not show a simple correlation with the electronegativities of the substituent groups. For example, the carbonyl oxygen 1s binding energies of methyl carbonate, formaldehyde, and carbonyl fluoride increase in the order $(\text{CH}_3\text{O})_2\text{CO} < \text{H}_2\text{CO} < \text{F}_2\text{CO}$. The present study was carried out to test the hypothesis that this apparently anomalous behavior is due to different electronic relaxation energies in the photoionizations. We have determined the core binding energies of a wide variety of carbonyl compounds to provide sufficient data for systematic analysis. Our experimental results, as well as some from other sources, are presented in Table I. In our analysis of these data we have assumed that, in most of the compounds, core ionization of the carbonyl oxygen atoms involves "extra" relaxation energy due to π electron donation from the substituent groups. Using two different approaches, we have evaluated the relative π donor abilities of the various substituent groups.

The Proximity Effect

The core binding energy of an atom in a molecule changes when other atoms in the molecule are replaced by different atoms or groups. These chemical shifts in binding energy are generally more pronounced the nearer the substituent groups are to the core-ionizing atom. This proximity effect can be seen in the carbon 1s binding energies of compounds of the type

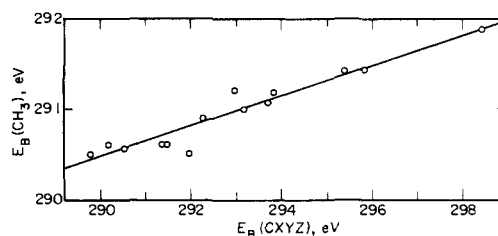
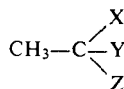


Figure 1. Plot of CH₃ carbon 1s binding energies vs. CXYZ carbon 1s binding energies for compounds of the type CH₃CXYZ. Note that the vertical scale is twice as great as the horizontal scale. The points, in order of increasing $E_B(\text{CXYZ})$, correspond to BEt_3 , BEt_2Cl , C_2H_6 , Et_3NBH_3 , Et_2NBH_2 , $\text{B}(\text{OEt})_3$, EtOH , $\text{EtO}(\text{CO})\text{CF}_3$, EtF , CH_3COCH_3 , CH_3CHO , $\text{CH}_3\text{CO}_2\text{H}$, CH_3CHF_2 , and CH_3CF_3 . For sources of data, see ref 1-5.

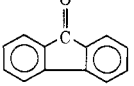
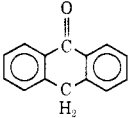
As the groups X, Y, and Z are changed, the binding energy of the CH₃ carbon atom changes much less than that of the CXYZ carbon atom. Figure 1 is a plot of the CH₃ binding energies against the CXYZ binding energies for 14 different compounds.¹⁻⁵ The data are linearly correlated and may be represented by the relation

$$E_B(\text{CH}_3) = 242.57 + 0.165E_B(\text{CXYZ}) \quad (1)$$

This behavior is typical of simple compounds in which the atoms whose binding energies are being compared are joined by single bonds.

An entirely different result is obtained from a comparison of the oxygen and carbon binding energies of carbonyl compounds in Table I. A plot of the oxygen binding energies

Table I. Oxygen 1s and Carbon 1s Binding Energies of Carbonyl Compounds

| Compound | $E_B(O)$, eV | $E_B(C)$, eV | π -Donor relaxation energy, eV ^a | |
|---|-----------------------|---------------------|---|---------------|
| | | | From Fig 2 | CHE-LEQ calcn |
| O=C=O | 541.30 ^{c,d} | 297.5 ^b | 0.5 | 0.7 |
| FC(=O)F | 540.60 | 299.47 | 2.5 | 3.7 |
| CF ₃ C(=O)CF ₃ | 540.51 | 295.61 | -0.1 | 0.6 |
| O=C=C=C=O | 539.8 ^e | 294.9 ^e | 0.1 | 0.8 |
| ClC(=O)Cl | 539.55 | 296.58 | 1.6 | 1.7 |
| CF ₃ C(=O)OH | 539.46 ^f | — | — | 1.9 |
| HC(=O)H | 539.43 ^{f,h} | 294.21 ^g | 0.0 | 0.4 |
| HC(=O)OH | 538.89 ^{f,h} | 295.86 ^g | 1.7 | 1.8 |
| (CH ₃) ₃ CC(=O)-Cl | 538.65 | 294.62 | 1.1 | 1.7 |
| CH ₃ C(=O)OC(=O)CH ₃ | 538.44 | 295.26 | 1.7 | 2.1 |
| CH ₃ C(=O)H | 538.4 | 293.83 | 0.8 | 1.3 |
| HC(=O)OCH ₃ | 538.35 ^f | — | — | 2.2 |
| CH ₃ C(=O)OH | 538.22 ^f | 295.4 ^b | 2.1 | 2.3 |
| <i>p</i> -NO ₂ C ₆ H ₄ C(=O)H | 538.21 | — | — | 2.0 |
| CH ₂ =CHC(=O)H | 538.03 | 293.59 | 1.0 | 1.8 |
| CH ₂ =CHOC(=O)CH ₃ | 538.00 | 294.80 | 1.9 | 2.6 |
| CH ₃ C(=O)-CH ₃ | 537.91 | 293.71 | 1.2 | 1.8 |
| CH ₃ OC(=O)-OCH ₃ | 537.88 | 295.95 | 2.8 | 3.2 |
| C ₆ H ₅ OC(=O)-OC ₆ H ₅ | 537.87 | — | — | 3.5 |
| <i>o</i> -HOC ₆ H ₄ C(=O)H | 537.8 | — | — | 2.4 |
| CH ₃ C(=O)-OCH ₃ | 538.35 ^f | — | 2.8 | — |
| <i>p</i> -ClC ₆ H ₄ C(=O)H | 537.62 | 293.31 | 1.2 | 2.3 |
| NH ₂ C(=O)H | 537.60 | 294.31 | 1.9 | 2.4 |
| C ₆ H ₅ C(=O)-OC ₂ H ₅ | 537.6 ^b | 294.5 ^b | 2.0 | 2.3 |
| C ₆ H ₅ C(=O)H | 537.52 | 293.17 | 1.2 | 2.4 |
| C ₆ H ₅ C(=O)-CH ₃ | 537.16 | 293.11 | 1.5 | 2.7 |
| (C ₆ H ₅) ₂ CH=CHC(=O)H | 537.14 | — | — | 2.8 |
|  | 537.13 | 292.3 | 1.7 | 2.9 |
| NH ₂ C(=O)-NH ₂ | 537.05 | 294.70 | 2.7 | 3.1 |
| <i>p</i> -CH ₃ OC ₆ H ₄ -C(=O)H | 536.98 | — | — | 3.0 |
| (CH ₃) ₂ NC(=O)H | 536.81 | 293.31 | 2.0 | 3.1 |
| C ₆ H ₅ C(=O)-C ₆ H ₅ | 536.80 | 292.9 | 1.7 | 3.2 |
|  | 536.75 | 293.4 ± 0.5 | 2.1 | 3.2 |

^a In this table, a positive relaxation energy corresponds to a negative contribution to the binding energy. ^b Reference 5. ^cG. Johansson, J. Hedman, A. Berndtsson, M. Klasson, and R. Nilsson, *J. Electron Spectrosc. Relat. Phenom.*, 2, 295 (1973). ^dR. W. Shaw, Jr., and T. D. Thomas, *J. Electron Spectrosc. Relat. Phenom.*, 5, 1081 (1974). ^eU. Gelius, C. J. Allan, D. A. Allison, H. Siegbahn, and K. Siegbahn, *Chem. Phys. Lett.*, 11, 224 (1971). ^fB. Mills and D. A. Shirley, unpublished observations. ^gT. D. Thomas, unpublished data. ^hT. X. Carroll, S. R. Smith, and T. D. Thomas, *J. Am. Chem. Soc.*, 97, 659 (1975).

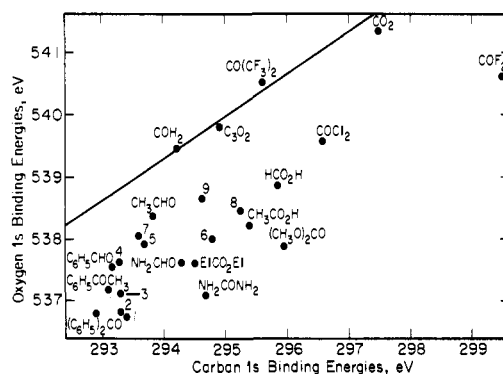
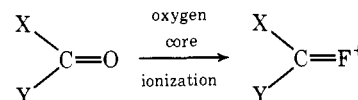
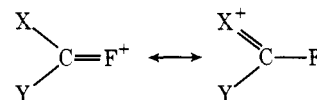


Figure 2. Plot of carbonyl oxygen 1s binding energies vs. the corresponding carbonyl carbon 1s binding energies. The numbered points correspond to the following compounds: 1, anthrone; 2, dimethylformamide; 3, fluorone; 4, *p*-chlorobenzaldehyde; 5, acetone; 6, vinyl acetate; 7, acrylaldehyde; 8, acetic anhydride; 9, pivaloyl chloride. See text for the significance of the line.

against the carbon binding energies (Figure 2) shows that there is essentially no correlation between these quantities. We believe the lack of correlation is caused by differences in the oxygen relaxation energies due to the different π -donor abilities of the groups attached to the carbonyl groups. If there were no shift in π electron density from the substituents to the oxygen of the carbonyl group, the oxygen core ionization would be represented by the equation

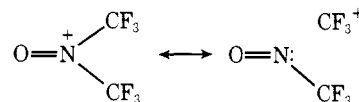


in which the ionized oxygen core is represented by the chemically equivalent⁶ fluorine core. However, because of the high electronegativity of the fluorine atom, it is more realistic to represent the core-ionized molecule as a resonance hybrid:



We shall refer to the shift in π electron density which increases the extent to which the right-hand resonance structure contributes to the bonding of the core-ionized molecule as π -donor relaxation.

The straight line in Figure 2 corresponds to the correlation expected for hypothetical molecules in which there is no π -donor relaxation in the carbonyl oxygen core ionization. Vertical deviations of the points in Figure 2 from this line correspond to π -donor relaxation energies (listed in Table I) and are measures of the π -donor abilities of the groups. The straight line was drawn in accord with the following theoretical considerations. First, the line should pass through the point for formaldehyde, because hydrogen atoms have no π -donor ability. Second, we believe it is a good approximation to assume that the CF₃ groups in (CF₃)₂CO also have no π -donor ability, inasmuch as π donation from a CF₃ group implies unlikely resonance structures such as $>\text{C}=\text{CF}_2 \text{F}^+$. However, core ionization of the carbonyl carbon atom in (CF₃)₂CO may well include a significant amount of extra relaxation, in view of the probable importance of the following type of resonance in the core-ionized molecule.^{7,8}



Such relaxation is probably unimportant in the other carbonyl compounds, and therefore we believe the carbonyl carbon binding energy for (CF₃)₂CO may be anomalously low. For

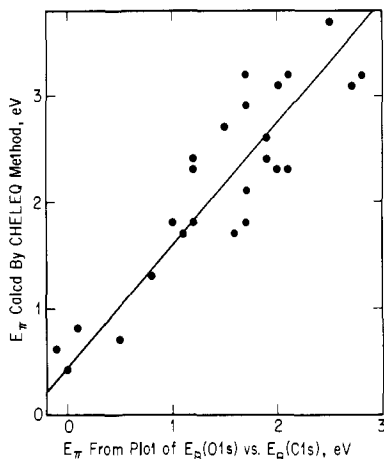
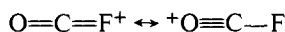


Figure 3. Plot of π -donor relaxation energies calculated using CHELEQ charges and eq 3 vs. π -donor relaxation energies obtained from Figure 2.

these reasons we feel that the point for $(\text{CF}_3)_2\text{CO}$ should lie on, or somewhat to the left of, the straight line. Third, in the case of CO_2 , oxygen core ionization should involve considerable π -donor relaxation:



Hence the CO_2 point should lie well below the straight line. It can be seen that the placement of the straight line in Figure 2 is consistent with the three restrictions we have just discussed. Indeed, the restrictions permit very little leeway in the placement of the line. The line corresponds to the correlation

$$E_B(\text{O}) = 333.5 + 0.7E_B(\text{C}) \quad (2)$$

The fact that the coefficient 0.7 is much greater than the corresponding coefficient 0.165 in eq 1 is probably due to three facts: (1) The $\text{C}=\text{O}$ bond is shorter than the $\text{C}-\text{C}$ bond in CH_3CXYZ ; hence changes in the charge of the carbon atom will have a relatively large effect on the potential at the oxygen core. (2) The $\text{C}=\text{O}$ double bond is more polarizable than the $\text{C}-\text{C}$ bond in CH_3CXYZ ; hence changes in the charge of the carbon atom will cause a relatively large change in the charge of the oxygen atom. (3) The oxygen atom is smaller than the carbon atom, and hence a given change in atomic charge will cause a greater change in 1s binding energy in the case of oxygen than in the case of carbon.

CHELEQ Analysis

We have used a second, entirely different method for estimating the "extra" relaxation energy associated with the oxygen core ionization of carbonyl compounds. The core binding energy of an atom can be calculated by the "transition-state" point-charge potential equation,⁹

$$E_B = k(Q + Q_f - 1)/2 + (V + V_f)/2 + I \quad (3)$$

where Q is the initial charge on the atom, V is the Coulombic potential energy due to the other charged atoms in the molecule, Q_f and V_f are the values of Q and V for the core-ionized molecule, and k and I are empirical constants. We have successfully correlated binding energies with eq 3 using atomic charges calculated by the CHELEQ electronegativity equalization method; the calculations for core-ionized molecules involved the equivalent-cores approximation.⁶ The k and I values for oxygen were determined from data for compounds which have no ambiguities in bonding and no special relaxation energy effects.¹⁰ We have calculated the oxygen 1s binding energies of the carbonyl compounds in Table I using these values of k and I and assuming that the core-ionized molecules

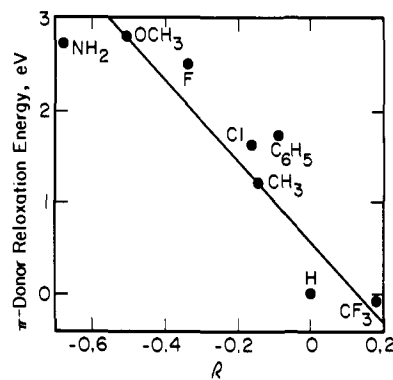


Figure 4. Plot of π -donor relaxation energies obtained from Figure 2 for compounds of the type X_2CO vs. resonance constants for the groups X . Resonance constants are from ref 11.

have the same simple valence-bond structures as the ground-state molecules (that is, assuming no π -donor relaxation). All of the calculated binding energies were greater than the experimental values; the differences are interpreted as π -donor relaxation energies and are listed in Table I. The values calculated in this way are similar to the values obtained from Figure 2. The two sets of data are plotted against one another in Figure 3 to show their correlation. Either set of π -donor relaxation energies listed in Table I may be used to compare the relative π -donor abilities of atoms and groups. However, in order to make meaningful comparisons, the values from a given set should be consistently used.

The assumption that the ground state of a carbonyl compound is fairly well represented by a single valence bond structure, with π bonding restricted to the $\text{C}=\text{O}$ bond, is supported by the binding energies of the atoms directly bonded to the carbonyl group. The core binding energies of these atoms are in good agreement with the values calculated by eq 3 using the appropriate k and I values and the CHELEQ method. For example, $E_B(\text{calcd}) - E_B(\text{exptl})$ for the fluorine atoms in F_2CO is -0.49 eV, for the chlorine atoms in Cl_2CO is 0.12 eV, and for the methoxy oxygen atoms in $(\text{CH}_3\text{O})_2\text{CO}$ is 0.26 eV. These differences are small compared to those given in the fifth column of Table I.

Comparison with R Values

Swain and Lupton¹¹ have used a large number of kinetic, thermodynamic, and spectroscopic data to evaluate the magnitudes of the "resonance constant" R for a series of substituents. The scale of R values was set up such that negative values correspond to substituents which are better π donors than the hydrogen atom and positive values correspond to substituents which are better π acceptors than the hydrogen atom. In Figure 4 the π -donor relaxation energies evaluated from Figure 2 for compounds of the type X_2CO are plotted against the R values for the X substituents. The fact that we observe a correlation of the type expected lends credence to our interpretation of the core electron binding energy data. We believe that π -donor relaxation energies derived by the methods we have outlined should have numerous chemical applications.

Experimental Section

All spectra were obtained for samples in the gas phase, using the Berkeley iron-free magnetic spectrometer and procedures which have been described previously.^{12,13} The compounds studied were commercial samples. Except for the gaseous and highly volatile compounds (which were purified by fractional condensation on the vacuum line), the compounds were used as received. All the compounds used were shown to be of satisfactory purity by vapor pressure measurement (agreement with literature values to within $\pm 5\%$), by melting point measurement (agreement with literature values to within $\pm 2^\circ$), or by NMR spectroscopy (impurities estimated to be less than 1%).

Acknowledgments. This work was supported by the National Science Foundation (Grant GP-41661X) and the U.S. Energy Research and Development Administration. We wish to thank Bernice Mills and David A. Shirley for providing binding energy data in advance of publication.

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Bis(fulvalene)diiron, Its Mono- and Dications. Intramolecular Exchange Interactions in a Rigid System

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Abstract: Biferrocenylene [bis(fulvalene)diiron, BFD] was synthesized by two independent routes: an Ullman coupling of dibromoferrocene and the reaction of the fulvalene dianion with ferrous chloride. It was chemically oxidized to the mixed valence monocation and to the dication. These derivatives were characterized by optical, Mössbauer, ESR, and x-ray photoelectron spectra and magnetic susceptibility. The Mössbauer spectra of the mixed valence salts at 298 and 77 K indicate that both iron atoms are equivalent. X-Ray photoelectron spectra similarly attest to this equivalence. An asymmetry in the intensity of the Mössbauer lines is due to a Karyagin effect. The Mössbauer spectrum of the dication shows a quadrupole splitting of 3.0 mm/s which is unusually large for a ferrocenium-type derivative. The magnetic susceptibility of BFD (2,3) picrate, measured in the 2-300 K range, follows a Curie law with a room temperature moment very close to the spin-only value. The dicationic fluoroborate salt is diamagnetic. The ESR spectra of the monocationic picrate and fluoroborate salts are characterized by narrow lines and a small rhombic anisotropy. An absorption in the near-infrared centered at 1550 nm is observed in the spectra of the monocations, but not the neutral or dicationic derivatives. The assignment of this band is discussed with respect to the results of the other physical measurements.

By definition, mixed valence compounds contain two or more atoms of the same element in different formal states of oxidation.² Theory³ predicts that new (e.g., magnetic and spectroscopic) properties will arise from interactions between valence electrons in unique oxidation states. Many inorganic mixed valence systems have been found to possess properties beyond those derived by simple addition from the component parts of the molecule.⁴

The term "mixed valence" was chosen by Robin and Day^{3b} with the intent that it be all encompassing. Systems ranging from no interaction and firmly trapped valences to complete delocalization and nonintegral valences are included. The former group is termed class I; the latter is class III. An intermediate classification, class II, houses those compounds in which there is some delocalization, but the properties of the components are still discernible.

Our objective has been to investigate the variation of properties with change in structure in binuclear mixed valence metallocenes. According to the theory of Hush,^{3a} the rate of electron transfer in mixed valence systems depends on the amount of reorganizational energy necessary to make the mixed valence sites identical; i.e., if the coordination geometry

of the two sites is very different, the rate of transfer is very slow. In this regard, the iron group metallocenes are notable candidates for rapid electron transfer since crystallographic data on ferrocene⁵ and ferrocenium salts⁶ have shown that the oxidation state of iron has a small effect on interatomic distances.

The organometallic mixed valence compound biferrocene [Fe(II)Fe(III)] picrate (Ib) has been characterized as a class II species.² Its Mössbauer,⁷ ESCA,⁸ magnetic,⁹ and optical¹⁰ properties have features attributable to the constituent ferrocene and ferrocenium portions in addition to features ascribable to its mixed-valence nature. Moreover, the fully oxidized biferrocene [2Fe(III)] salt (Ic), although unstable in solution and more difficult to characterize, displays properties that are essentially the sum of two ferrocenium units.^{7,9} This is in sharp contrast to the observed behavior of the mono- (IIB) and dioxidized (IIC) salts of biferrocenylene (bis(fulvalene)diiron, BFD), whose syntheses and properties are discussed herein.

Synthesis

Bis(fulvalene)diiron (IIa) has been reported in the literature as a product of the Ullmann coupling of 1,1'-diiodoferrocene¹¹