

CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, NORTHWESTERN UNIVERSITY, EVANSTON, ILLINOIS 60201,
AND THE UNIVERSITY OF BIRMINGHAM, BIRMINGHAM, ENGLAND

Photoionization Studies of Metal Carbonyls. I. Ionization Potentials and the Bonding in Group VI Metal Hexacarbonyls and in Mononuclear Carbonyls and Nitrosyl Carbonyls of Iron, Cobalt, and Nickel^{1a}

BY D. R. LLOYD^{1b} AND E. W. SCHLAG^{1c}

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Adiabatic and vertical ionization potentials (IP) have been measured, using a photoionization spectrometer, for the hexacarbonyls of chromium, molybdenum, and tungsten and for iron pentacarbonyl, nickel tetracarbonyl, cobalt nitrosyl tricarbonyl, and iron dinitrosyl dicarbonyl, and upper limits to the bond energies in the molecular ions have been deduced. Photoelectron spectral data are also presented for iron pentacarbonyl and nickel tetracarbonyl. Previous ionization values for these molecules are compared with the new values, and the data are discussed in terms of simple molecular orbital schemes for the uppermost occupied orbitals. It is shown that the results may be interpreted in terms of strong π "back-donation" from metal to ligand, which for the hexacarbonyls increases in the sequence $\text{Mo}(\text{CO})_6 < \text{Cr}(\text{CO})_6 < \text{W}(\text{CO})_6$. Correlations with other bonding data are discussed and a rationalization of this sequence is suggested. It is also proposed that the charges on the metal atoms in all of these compounds are probably close to zero.

Introduction

At the time of beginning this work, two sets of determinations of the ionization potentials of the monomeric carbonyls of chromium, molybdenum, tungsten, iron, and nickel had been made. The work of Vilesov and Kurbatov,² referred to subsequently as VK, used the photoionization method; that of Winters and Kiser³ (WK) employed electron impact in a conventional mass spectrometer. The two sets showed reasonable agreement for chromium and molybdenum hexacarbonyls, but there was an appreciable discrepancy for the tungsten compound, with larger discrepancies for iron pentacarbonyl and nickel tetracarbonyl. We decided to reinvestigate these compounds using a newly constructed photoionization spectrometer⁴ in the hope of understanding the discrepancies. We have also examined cobalt nitrosyl tricarbonyl and iron dinitrosyl dicarbonyl, which form with nickel tetracarbonyl an isoelectronic and essentially isostructural⁵ sequence. Since we began this work further electron impact studies of the compounds have appeared, by Foffani, *et al.*,^{6,7} (F), Bidinosti and McIntyre⁸ (BM), Schildcrout, Pressley, and Stafford⁹ (S), and Junk and Svec¹⁰ (JS). Few of the ionization potentials reported in these studies

are in agreement with each other at one standard deviation and many do not agree at two or three standard deviations.

Experimental Section and Data Treatment

Compounds.—These were all provided by Professor F. Basolo and his coworkers and were vacuum distilled or sublimed before use.

Photoionization Spectrometers.—Except for nickel carbonyl, the photoionization experiments were all carried out at 10^{-8} – 10^{-4} mm in an automatically recording spectrometer which is described in detail elsewhere.⁴ Briefly, vacuum ultraviolet continuum radiation, from microwave discharges in krypton or xenon, is dispersed by a grating monochromator and is passed through the vapor of the substance being examined. The vapor flows continuously through the apparatus at a pressure between 10^{-8} and 10^{-4} mm. Positive ions produced by the radiation are counted and the ion count rate, divided by the transmitted photon beam intensity, is displayed on a recorder. The wavelength drive on the monochromator is linear with time so that the recorder trace is a plot of relative ionization cross section¹¹ against wavelength. No search for negative ions was made. The photon energy limit of the instrument is determined by the cutoff of the lithium fluoride windows employed at about 1050 Å, 11.8 eV, but also in this work by the limit of the krypton continuum radiation⁴ at 1250 Å, 9.9 eV. The measurements on nickel carbonyl were made at a higher pressure, ~ 1 mm, with a manual instrument. The same light source and monochromator as in the recording instrument were used, but the ionization current flowing between two collector plates with a potential difference of about 20 V was measured by a Cary Model 30 vibrating-reed electrometer. The transmitted beam intensity was measured by allowing it to fall on a sodium salicylate phosphor and detecting the fluorescent radiation with an EMI 6097B photomultiplier operated at 1.1 kV and a Victoreen electrometer, Type VTE1. Readings of the two currents and their ratio were made at 1-Å intervals through the threshold region and 5-Å intervals above this region.

Iron pentacarbonyl was examined in the threshold region by both techniques, using a krypton continuum light source, and within experimental error identical values of the ionization onset were obtained.

Photoelectron Spectrometer.—The photoelectron spectra were obtained on an instrument recently built at Birmingham. Me-

(1) (a) Most of the experimental work was carried out at Northwestern University; a partial report was given at the meeting of The Chemical Society of London at Brighton, Sussex, Sept 21–22, 1966. (b) University of Birmingham; author to whom correspondence should be addressed. (c) Northwestern University; Alfred P. Sloan Fellow.

(2) F. I. Vilesov and B. L. Kurbatov, *Dokl. Akad. Nauk SSSR*, **140**, 1364 (1961).

(3) (a) R. E. Winters and R. W. Kiser, *Inorg. Chem.*, **4**, 157 (1965); (b) *ibid.*, **3**, 699 (1964).

(4) E. W. Schlag and D. R. Lloyd, in preparation.

(5) "Interatomic Distances," The Chemical Society, London, 1958, pp M121, M143, M178.

(6) A. Foffani, S. Pignataro, B. Cantone, and F. Grasso, *Z. Physik. Chem. (Frankfurt)*, **45**, 79 (1965).

(7) A. Foffani, S. Pignataro, G. Distefano, and G. Innorta, *J. Organometal. Chem. (Amsterdam)*, **7**, 473 (1967).

(8) D. R. Bidinosti and N. S. McIntyre, *Can. J. Chem.*, **45**, 641 (1967).

(9) S. M. Schildcrout, G. A. Pressley, and F. E. Stafford, *J. Am. Chem. Soc.*, **89**, 1617 (1967).

(10) G. A. Junk and H. J. Svec, *Z. Naturforsch.*, **23b**, 1 (1968).

(11) A. J. C. Nicholson, *J. Chem. Phys.*, **39**, 954 (1963), Appendix II.

chanically this instrument is similar to that described by Al-Joboury and Turner,¹² but the inner grid is replaced by a stack of plates perpendicular to the photon beam so that vertical ionization potentials may be obtained. The differential spectra are obtained by an ac modulation of the swept electron retarding potential. Since the signals were quite weak a relatively large modulation of 300 mV was used, so that the energy resolution is about 0.3 eV. The voltage scale was calibrated using the ionization of krypton with an equal modulation.

Determination of the Ionization Onset.—The approximate position of an onset may be determined by visual inspection of the data, but the exact position at which the curve begins to rise is confused by noise on the trace. The procedure adopted for a first onset was to draw a horizontal line through the noise for 50–100 Å below the approximate onset and then to draw a straight line through the region in which the curve rises above the horizontal line by two or three times the average noise level. The second line was drawn as a tangent to the rising curve, and the intersection of the two lines was taken as the apparent ionization onset. At least six curves were analyzed for each compound and an average and standard deviation were calculated. Such an apparent onset is displaced to lower energy from the true one by half the half-width of the radiation emerging from the monochromator,¹³ and the values of onsets reported in this paper have been corrected for this. Later ionization onsets were determined similarly except that the first line below the onset is usually not horizontal; it is drawn as a tangent to the curve below the onset.

Differentiation of Ionization Onset and Adiabatic Ionization Potential When Vibrational Structure Is Not Resolved.—All of the molecules examined here have several vibrational modes for which excited states will be considerably populated at room temperature, so the ionization onset may be at lower energy than the adiabatic IP because of ionization of vibrationally excited molecules. Some workers¹⁴ have corrected for this effect by plotting the logarithm of ionization probability against energy and taking the adiabatic IP as the position at which the semilogarithmic plot shows a break. An analysis of this procedure suggests that a break is not necessarily observed, but if one is observed, then this is a better approximation to the adiabatic IP than the ionization onset but may still be in error by as much as 0.1 eV. Such a break does not need correction for the monochromator resolution. Photoionization data for all of the compounds examined, except for the hexacarbonyls, have been replotted on a semilogarithmic scale through the threshold region.

Results

(a) **Hexacarbonyls.**—Figure 1 shows the ionization probability curves for $\text{Cr}(\text{CO})_6$, $\text{Mo}(\text{CO})_6$, and $\text{W}(\text{CO})_6$. In all three compounds a well-defined step is observed in the curve, followed by a second ionization process close to the limit of the instrument. Slow scans through the steps for all three compounds show evidence of some structure, and although the variations from a smooth curve are not much bigger than the noise level on the trace, the inflection positions are quite reproducible. An experimental trace for $\text{W}(\text{CO})_6$ is shown in Figure 2. The slight dips, marked X, are due to emission lines in the light source. The arrows mark the average position of the inflection points determined for six to ten runs and the values of ionization energy measured from these inflection points are given in Table I. It is seen that the large "step" of Figure 1 includes a set of steps of gradually changing

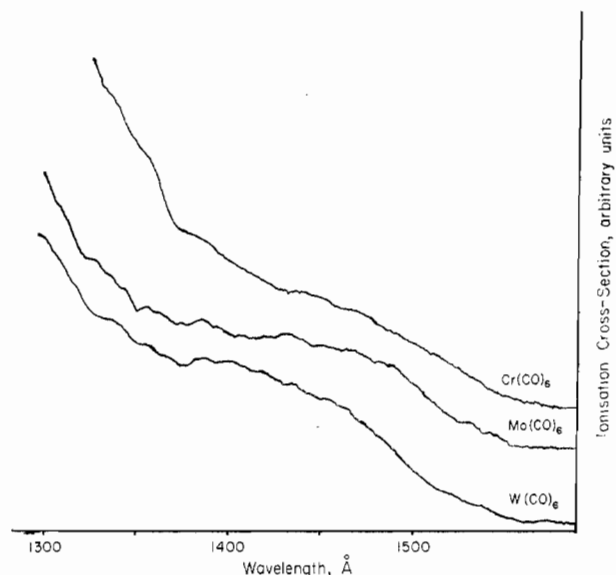


Figure 1.—Relative ionization cross-section plots against wavelength for hexacarbonyls of chromium, molybdenum, and tungsten.



Figure 2.—Relative ionization cross-section plot against wavelength for tungsten hexacarbonyl in the region of the onset. The dips in the curve, marked X, are due to the presence of emission lines in the continuum light source used. The arrows indicate the position of inflections averaged over several runs.

height, consistent with the production of vibrationally excited ions from a ground-state molecule, and a first step of much smaller height. The most reasonable interpretation of this small step is that it is due to the ionization of vibrationally excited molecules, a so-called "hot band." From Table I it is seen that for all three compounds, within experimental error, the separation of this small step from the first large one (0.10, 0.08, 0.08 eV) is the same as the average spacing of the sequence of steps (0.09, 0.10, 0.10 eV), and it therefore seems reasonable to suggest that the same vibration, in the molecule and in the ion, is responsible for all of the steps. Examination of the infrared spectra¹⁵ for the three carbonyls shows that only one fundamental vibration is of comparable energy to this separation, the ν_7 of T_{1u} symmetry ($\text{Cr}(\text{CO})_6$, 0.083 eV; $\text{Mo}(\text{CO})_6$, 0.074 eV; $\text{W}(\text{CO})_6$, 0.073 eV). It is interesting, and

(12) M. I. Al-Joboury and D. W. Turner, *J. Chem. Soc.*, 5141 (1963).

(13) E. Murad and M. G. Ingiram, *J. Chem. Phys.*, **40**, 3263 (1964).

(14) K. Watanabe, T. Nakayama, and J. Mottl, "Final Report on Ionization Potentials of Molecules by a Photoionization Method," Report OOR 1624, Office of Technical Services, Washington, D.C., 1959.

(15) L. H. Jones, *Spectrochim. Acta*, **19**, 329 (1963).

TABLE I
IONIZATION ENERGIES^a FOR GROUP VI HEXACARBONYLS

	Cr(CO) ₆	Mo(CO) ₆	W(CO) ₆
First Large Step			
"Hot band" ^b	8.042 ± 0.014	8.146 ± 0.012	8.162 ± 0.012
Adiabatic IP ^b	8.142 ± 0.017	8.227 ± 0.011	8.242 ± 0.006
Later inflections	8.24	8.30	8.32
	8.33	8.40	8.41
	8.41	8.52	8.52
		8.63	8.56
			8.76
			8.81
Vertical IP	8.38 ± 0.02	8.35 ± 0.07	8.60 ± 0.03
Second Rise			
First inflection	9.26	9.21 ± 0.03	9.43
Later inflections	9.43	9.44	9.58
	9.59	9.58	9.78
	9.79	9.78	
		9.91	
		10.04	
Data from Earlier Work			
Photoionization ^c	8.03 ± 0.03	8.12 ± 0.03	8.18 ± 0.03
Electron impact IP			
WK ^d	8.15 ± 0.17	8.23 ± 0.12	8.56 ± 0.13
F ^e	8.18 ± 0.07	8.30 ± 0.03	8.46 ± 0.02
BM ^f	8.48 ± 0.08	8.46 ± 0.08	8.47 ± 0.1
JS ^g	8.44 ± 0.05	8.43 ± 0.05	8.48 ± 0.05
Electron impact AP of M(CO) ₆ ⁺			
WK ^d	(9.5)	9.80 ± 0.15	9.80 ± 0.17
F ^e	9.17 ± 0.04	9.64 ± 0.05	9.97 ± 0.04
BM ^f	8.95 ± 0.1	9.43 ± 0.1	9.86 ± 0.1
JS ^g	9.32	9.14	9.21

^a All energies in electron volts; unless otherwise stated the standard deviations for this work, from eight to ten determinations just above the first onset and five to six elsewhere, may be taken as ±0.02 eV. ^b See text for explanation. ^c Reference 2. ^d Reference 3. ^e Reference 6. ^f Reference 7. ^g Reference 10.

possibly significant, that this is by far the most intense infrared absorption outside the C–O stretch region. If the weak step in the ionization spectrum is a hot band, and the first stronger step is the adiabatic ionization potential, then the ratio of intensities of these steps should be the same as the Boltzmann population ratio for excited and ground-state molecules. Measurement of heights from the curve is not very accurate because of the noise level, but the ratio has been estimated as ~1:8. At 300°K the population ratios for ν_7 for the chromium, molybdenum, and tungsten compounds are 1:7.2, 1:5.2, 1:4.5, in reasonable agreement considering the inaccuracy of measurement. On this basis it is considered that the first strong step is the 0–0 adiabatic ionization potential, and the weak step is the 0–1 "hot band."

The second rise on each ionization curve occurs at the bottom of the range of values reported for the electron impact determination of the appearance potential (AP) for the production of the fragment ions M(CO)₅⁺ (see Table I). This second rise is most unlikely to be due to ionization from a deeper lying orbital of M(CO)₆ since calculations^{16,17} indicate that the energy separation of the first two sets of occupied orbitals should be about 5 eV for all three compounds, and this has been confirmed¹⁷ by photoelectron spectroscopy for Cr(CO)₆. If this second onset at about 9 eV is taken as the true AP of M(CO)₅⁺, then the difference

between this value and the adiabatic IP of M(CO)₆ gives an upper limit¹⁸ to the M–C bond energy in M(CO)₆⁺. These values are given in Table II together with bond energies for the neutral molecules, determined^{19,20} as activation energies for the first-order gas-phase exchange reaction with ¹⁴CO, and some infrared spectroscopic data.¹⁵ Inflections are observed on this second rise also, and they are recorded in Table I.

TABLE II
BONDING PARAMETERS IN GROUP VI HEXACARBONYLS

	Cr(CO) ₆	Mo(CO) ₆	W(CO) ₆
Bond Energies, eV			
(OC) ₅ M ⁺ –CO ^a	1.12 ± 0.04	0.98 ± 0.04	1.19 ± 0.03
(OC) ₅ M–CO ^b	1.70 ± 0.02	1.34	1.75
Difference	0.58 ± 0.06	0.36	0.56
ΔIP, ^c eV	0.24 ± 0.04	0.12 ± 0.08	0.36 ± 0.04
Force Constants, ^d mdyn/Å			
M–C str	2.034	1.806	2.148
C–O str	17.873	18.122	17.695

^a Upper limit, determined from this work, see text and Table I. ^b References 19 and 20. ^c Difference of vertical and adiabatic IP from Table I. ^d Reference 15.

The vertical IP of a molecule is the energy required to remove an electron without change of nuclear geometry, and so will in general correspond to a transition to a fictitious state of the ion in between some pair of true vibrational states. This IP corresponds to the position of maximum rate of increase of ionization probability, *i.e.*, to the steepest point on the recorded curve. A smoothed curve was drawn through the noise and structure and the inflection point was estimated by drawing in the tangent to the curve. The vertical IP's recorded in Table I are the mean values of inflection points determined in this way.

(b) **Iron Pentacarbonyl, Nickel Tetracarbonyl, Cobalt Nitrosyl Tricarbonyl, and Iron Dinitrosyl Dicarboxonyl.**—For all four compounds the ionization probability curves are very similar except at the threshold, where both nickel and iron carbonyls show a break on a semilogarithmic plot but the nitrosyl carbonyls do not. The form above the threshold is illustrated by Figure 3, which shows an experimental curve for iron pentacarbonyl. The curve is almost featureless except that after a very gradual rise from threshold at A₁ a region which approximates to a straight line is observed, beginning at the point marked B on the figure, followed by a further rise beginning at A₂. Several studies of nickel tetracarbonyl and iron pentacarbonyl by mass spectrometry have been reported, and the details are given in Table III. The lowest reported value⁹ for the appearance potential of the fragment Ni(CO)₃⁺, 8.89 ± 0.15 eV, includes the value 9.03 ± 0.10 eV which we determine for the position of A₂, so we consider that the total curve is a composite of the ionization processes forming Ni(CO)₄⁺ and Ni(CO)₃⁺.

(18) E. Murad and M. G. Inghram, *J. Chem. Phys.*, **40**, 3263 (1964).

(19) G. Pajaro, F. Calderazzo, and R. Ercoli, *Gazz. Chim. Ital.*, **90**, 1846 (1960).

(20) G. Cetini and O. Gambino, *Atti Accad. Sci. Torino, Classe Sci. Fis., Mat. Nat.*, **97**, 1197 (1962–1963).

(16) N. A. Beach and H. B. Gray, *J. Am. Chem. Soc.*, **90**, 5713 (1968).

(17) K. G. Caulton and R. F. Fenske, *Inorg. Chem.*, **7**, 1273 (1968).

TABLE III
 IONIZATION POTENTIALS AND APPEARANCE POTENTIALS (eV)

	Fe(CO) ₅	Ni(CO) ₄	CoNO(CO) ₅	Fe(NO) ₂ (CO) ₂
	(1) Data from This Work			
First adiabatic IP ^a	7.96 ± 0.02	8.28 ± 0.01	8.11 ± 0.03	8.25 ± 0.12
First vertical IP	8.60 ± 0.04 ^b	8.93 ± 0.05 ^b	9.05 ± 0.17 ^c	9.01 ± 0.15 ^c
Second adiabatic IP ^a	9.50 ± 0.06 ^b	9.58 ± 0.05 ^b
Second vertical IP	9.86 ± 0.04 ^b	9.76 ± 0.06 ^b
Fragment AP ^a	8.62 ± 0.07	9.03 ± 0.10 ^d	9.37 ± 0.10	9.46 ± 0.09
	(2) Data from Earlier Work			
Photoionization ^e	7.95 ± 0.03	8.28 ± 0.03
Electron impact IP				
WK ^f	8.53 ± 0.2	8.64 ± 0.15
S ^g	...	8.35 ± 0.15
F ^h	8.14 ± 0.06	...	8.75 ± 0.1	8.45 ± 0.1
BM ⁱ	8.16 ± 0.05	8.57 ± 0.10
JS ^j	8.40 ± 0.03	8.75 ± 0.07
First electron impact fragment AP				
WK ^f	10.0 ± 0.2	9.36 ± 0.15
S ^g	...	8.89 ± 0.15
F ^h	8.34 ± 0.12
BM ⁱ	8.73 ± 0.08	9.22 ± 0.10
JS ^j	9.17	9.34

^a See text. ^b Photoelectron spectroscopy. ^c Probable lower limit; see text. ^d Single determination only. ^e Reference 2. ^f Reference 3. ^g Reference 9. ^h Reference 6 ((Fe(CO)₅) and reference 7 (CoNO(CO)₅, Fe(NO)₂(CO)₂). ⁱ Reference 8. ^j Reference 10; AP standard deviations within the range ±0.05 to ±0.20 eV.

Similarly, twice the standard deviation of the lowest reported onset⁶ for the fragmentation of Fe(CO)₅ to Fe(CO)₄⁺, 8.34 ± 0.12 eV, includes our value of 8.62 ± 0.07 eV, for the position of A₂. Accordingly A₂ is considered to be the fragmentation onset for all four compounds and is reported as such in Table III.

Although no fragmentation onset data are available for the nitrosyl carbonyls, the cracking patterns which have been reported⁷ show that a CO ligand is lost more readily than a NO ligand, and there is considerable evidence that CO is bound less strongly than NO in these molecules,²¹ so the fragmentation onset A₂ is assigned to loss of CO.

For nickel tetracarbonyl and iron pentacarbonyl, the adiabatic IP's reported in Table III are the positions of the breaks in the semilogarithmic plots, though the ionization onsets are appreciably lower, 8.19 ± 0.02 and 7.78 ± 0.02 eV, respectively. Since no breaks were observed for the nitrosyl carbonyls, the adiabatic IP's reported are ionization onset energies determined as in the Experimental Section. The straight-line portion of each ionization curve probably corresponds to the region of the vertical IP for the molecule. In the absence of interference from the fragmentation process the vertical IP is the midpoint of an approximately rectilinear portion (*cf.* section (a)), so the midpoint of the region B–A₂ on our curves is a probable lower limit to the true vertical IP. The first vertical IP's determined by photoelectron spectroscopy for the nickel and iron carbonyls are greater than these lower limits by 0.6 and 0.3 eV, respectively. No photoelectron data are available for the nitrosyl carbonyls

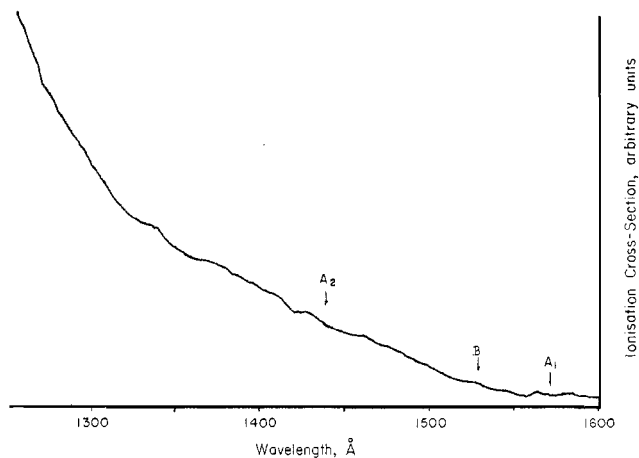


Figure 3.—Relative ionization cross-section plot against wavelength for iron pentacarbonyl. A₁ and A₂ signify the values assigned to the adiabatic ionization potential and to the onset of fragmentation of the molecular ion, respectively.

so the estimated lower limits for the vertical IP's for these compounds are reported in Table III.

(c) **Photoelectron Spectra of Nickel and Iron Carbonyls.**—The regions of the lowest ionization potentials for these two compounds are shown in Figure 4. No further peaks are observed until the region below 13.5 eV, where both compounds show complex spectra which are incompletely resolved under present conditions. Vertical IP's have been measured from the peak maxima and are reported in Table III. For both compounds the second photoelectron peak is resolved with no sign of interference from the strong ionization which appears in the photoionization spectra in the region after the first IP. This confirms our assignment of this strong ionization to a fragmentation process, since

(21) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, Interscience Publishers, New York, N. Y., 1966, p 720 ff.

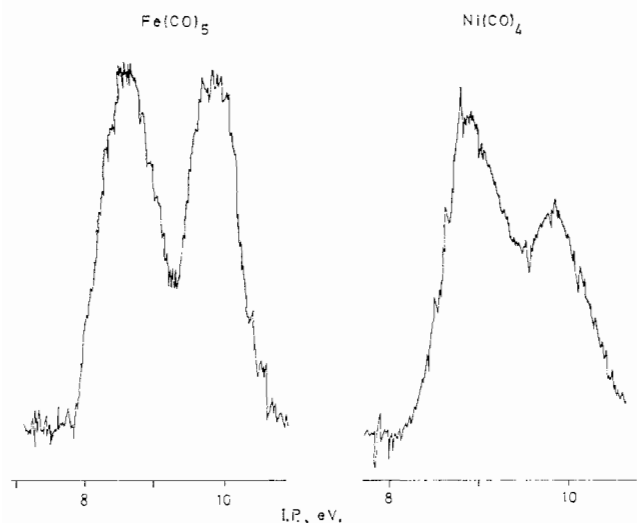


Figure 4.—The first two bands in the photoelectron spectra of iron pentacarbonyl and nickel tetracarbonyl.

the photoelectron experiment observes electrons which leave the ions in a time much shorter than that needed for decomposition. The onsets of the photoelectron peaks cannot be measured very accurately because of the low instrument sensitivity, but they have been estimated as 8.00 ± 0.08 and 9.50 ± 0.06 eV for $\text{Fe}(\text{CO})_5$ and as 8.24 ± 0.14 and 9.58 ± 0.05 eV for $\text{Ni}(\text{CO})_4$.

Discussion

Comparisons with Previous Data.—The carbonyls have all been previously examined by the photoionization method² and for all three hexacarbonyls the onsets of ionization determined here are in good agreement with the earlier data (see Table I). However, as discussed in the previous section, we believe that the onset of ionization represents a "hot band" and the true adiabatic IP is one vibrational quantum higher in energy. The previously reported ionization onsets² for iron and nickel carbonyls are in surprisingly good agreement with the adiabatic IP determined from the semilogarithmic plots (Table III).

We expect that when photoionization measurements are made with high sensitivity, it will often happen that the ionization onset will be at lower energy than the true adiabatic IP. This will be most likely to happen when the molecule has a number of vibrational degrees of freedom which are appreciably populated at room temperature. Except where the vibrational structure is resolved, this introduces an uncertainty into the measurements which is likely to be larger than the usual precision limits in such work, and this should be borne in mind when using photoionization data. However, any such errors are likely to be small in comparison with those in electron impact work.

The electron impact studies have given varying results for these compounds. In terms of our values for the hexacarbonyls, the appearance potentials reported by WK³ correspond very closely to adiabatic IP's for $\text{Cr}(\text{CO})_6$ and $\text{Mo}(\text{CO})_6$ and to the vertical IP for $\text{W}(\text{CO})_6$, though for the first two our vertical IP's

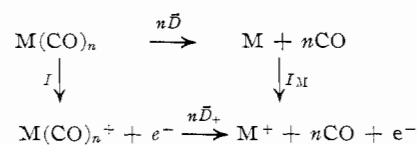
are also within two standard deviations. F⁶ reported an IP for $\text{Cr}(\text{CO})_6$ which is identical with that of WK, a value for $\text{Mo}(\text{CO})_6$ within the error limits of our vertical IP, and a value for $\text{W}(\text{CO})_6$ which is appreciably less than our vertical IP. Finally both BM⁸ and JS¹⁰ found the ionization potentials of all three compounds to be identical, very close to F's value for $\text{W}(\text{CO})_6$; however for each value twice the standard deviation includes our vertical IP.

Intercomparison of the electron impact studies of iron and nickel carbonyls shows variations in IP of up to 0.4 eV and almost all of the values are significantly (2σ) less than our vertical IP.

It may be concluded from this variety of results that the electron impact values represent complex functions of the instruments on which the values were determined, and that even within such a closely related set of compounds as the five carbonyls the errors on any one instrument may vary from one compound to another by at least 0.3 eV. This suggests that in general electron impact measurements cannot be expected to distinguish between adiabatic and vertical ionization potentials. It has been proposed²² that electron impact values are upper limits to adiabatic IP; this is borne out by these results.

The Bonding in Group VI Hexacarbonyls.—It is fairly generally accepted that the electronic structure of these compounds is well represented by a molecular orbital scheme^{17,23} in which a large contribution to the molecular binding comes from σ -type orbitals formed from overlap of the "lone-pair" orbital on the C atom of CO with metal s, p, and d (e_g) orbitals, with a concomitant transfer of electrons to the metal atom. There is strong evidence, particularly from infrared spectra,¹⁵ that there is also π bonding leading to transfer of charge in the opposite direction, from metal d (t_{2g}) orbitals to the π^* orbitals which are unoccupied in free CO. The $2t_{2g}$ orbitals, which are responsible for any such "back-donation" effects, are the highest lying occupied levels¹⁶ and so the first ionization process should be the ejection of an electron from these orbitals. The $1t_{2g}$ orbitals are essentially the CO π orbitals which in CO are about 2.9 eV below the σ lone pair.

Recently it has been claimed¹⁰ that some mass spectrometric measurements are "not consistent with extensive π bonding in metal carbonyls." The basis of this claim is that the energy calculated for dissociation of a carbonyl into a metal atom and free CO is less than that for dissociation of the carbonyl parent ion into a metal ion and free CO. This energy difference may be calculated from the cycle



(22) R. W. Kiser, "Introduction to Mass Spectrometry and Its Applications," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1965.

(23) H. B. Gray and N. A. Beach, *J. Am. Chem. Soc.*, **85**, 2922 (1963).

where I is the adiabatic IP of the carbonyl, I_M is the IP of the metal atom, and \bar{D} and \bar{D}_+ are the mean bond dissociation energies of the molecule and parent ion, respectively. The diagonal of the cycle corresponds approximately to the appearance potential of M^+ from $M(\text{CO})_n$, and equating the two paths shown for the production of M^+ , we have

$$I + n\bar{D}_+ = I_M + n\bar{D}$$

i.e., the difference in total dissociation energies $n(\bar{D} - \bar{D}_+)$ is equal to $I - I_M$. Values of this difference, calculated from our adiabatic IP and the spectroscopic values²⁴ of I_M , are: NiCO_4 , +0.55 eV; $\text{Fe}(\text{CO})_5$, +0.09 eV; $\text{Cr}(\text{CO})_6$, +1.38 eV; $\text{Mo}(\text{CO})_6$, +1.13 eV; $\text{W}(\text{CO})_6$, +0.26 eV. Since all of the available electron impact IP are higher than our adiabatic values, the corresponding differences are all higher than our values, *i.e.*, all of the measurements indicate a decrease in total dissociation energy upon ionization, not an increase. The reported increase¹⁰ seems to be the result of comparing calorimetrically determined \bar{D} values with \bar{D}_+ values obtained by subtracting I from the appearance potential of M^+ , even though it is probable¹⁰ that M^+ is produced in an excited state. The comparison used here is independent of the measurements upon the appearance potentials of M^+ and indicates that all of the molecules are destabilized by the first loss of an electron. In the case of the hexacarbonyls this indicates strong metal-carbon π bonding *via* the $2t_{2g}$ orbitals. However, the process of ionizing an electron localized more on the metal atom than on the ligands will make the metal atom more positive than the ligands. This will stabilize the metal atom orbitals, giving a better energy match with the ligand σ orbitals as well as a worse match with the ligand π^* orbitals, so in addition to a loss in π -bonding energy there is expected to be a gain in σ -bonding energy. Since the IP differences are all positive, the loss in π stabilization must be the more important of these two processes.

Further confirmation of the π bonding comes from comparison of the first dissociation energies for molecule and ion listed in Table II. For each of the hexacarbonyls the first dissociation energy of the ion is considerably (0.4–0.6 eV) less than that of the molecule. This difference is appreciably greater than the difference of mean bond dissociation energies, and this may be rationalized in terms of the competition of σ stabilization and π destabilization on ionization. The π bonding has the effect of delocalizing the $2t_{2g}$ electrons, so that the positive charge in $M(\text{CO})_6^+$ will be only partially localized on the central atom, and this delocalization will reduce the lowering of the metal orbital energies and the σ stabilization. As successive CO groups are lost from $M(\text{CO})_6^+$, it is probable that the charge delocalization will decrease, so there will

be greater σ stabilization and π destabilization for MCO on ionization than for $M(\text{CO})_6$. This will mean that the difference of average bond energies ($\bar{D} - \bar{D}_+$) will be less than the difference of first dissociation energies for $M(\text{CO})_6$ and $M(\text{CO})_6^+$.

If the σ stabilization effect is least for the first dissociation, then the decrease in the first bond energy upon ionization is a better index of π bonding than ($\bar{D} - \bar{D}_+$). Accordingly we deduce from the bond energies that the π stabilizations of $\text{Cr}(\text{CO})_6$ and $\text{W}(\text{CO})_6$ are approximately equal and greater than that of $\text{Mo}(\text{CO})_6$; however because of the unknown σ effects and also because our ion bond energy takes no account of possible kinetic energy of the fragments CO and $M(\text{CO})_6^+$, this only indicates a probable sequence.

An alternative measure of bonding character is given by the difference between adiabatic and vertical IP's for the compounds. This difference results from the change in equilibrium bond lengths upon removing bonding or antibonding electrons, with a corresponding maximum Franck-Condon factor for ionization to a vibrationally excited ion. For a stable polyatomic molecule the changes in distances are expected to be small, and so this description of bonding character is related to bond force constant rather than to bond energy. From Table II it is evident that the order of bonding characters measured in this way for the $2t_{2g}$ orbital is $\text{W} > \text{Cr} > \text{Mo}$. This may be compared with the force constants for these compounds also shown in Table II, where the same sequence is found in the M-C stretching force constants F_{MC} and the opposite sequence is found for the C-O stretching force constants F_{CO} . A strong interaction of the metal $d(t_{2g})$ orbitals with the CO π^* orbitals provides a reasonable rationalization both of the infrared spectra and of our ionization observations. Also this study and the infrared work are in full agreement that the order of increasing π back-donation is $\text{Mo}(\text{CO})_6 < \text{Cr}(\text{CO})_6 < \text{W}(\text{CO})_6$. It is possible that the sequence of activation energies for CO exchange is mainly due to this bonding sequence, since the (first) bond energies in the molecular ions, which have one less electron in the π -bonding orbitals, are very much closer to each other but still fall in the same sequence (Table II). However, there may also be differences in the σ bonding between the three compounds, and there will be considerable electronic reorganization during the bond-breaking processes, so we do not have a full explanation of the kinetic differences between the three compounds.

Comparison of Energy Levels in the Hexacarbonyls. Rationalization of the π -Bonding Sequence.—The electronic spectra for these three compounds have been reported and assigned in terms of a molecular orbital scheme.²³ Combination of the assigned spectral transitions with the vertical IP's for the $2t_{2g}$ orbital gives the quantitative mo diagrams for the upper orbitals shown in Figure 5 for all three compounds. In the construction of this diagram it has been assumed, except for the e_g orbitals, that a spectral transition corre-

(24) C. E. Moore, "Atomic Energy Levels," U. S. National Bureau of Standards Circular 467, U. S. Government Printing Office, Washington, D. C., 1949, 1952, and 1958.

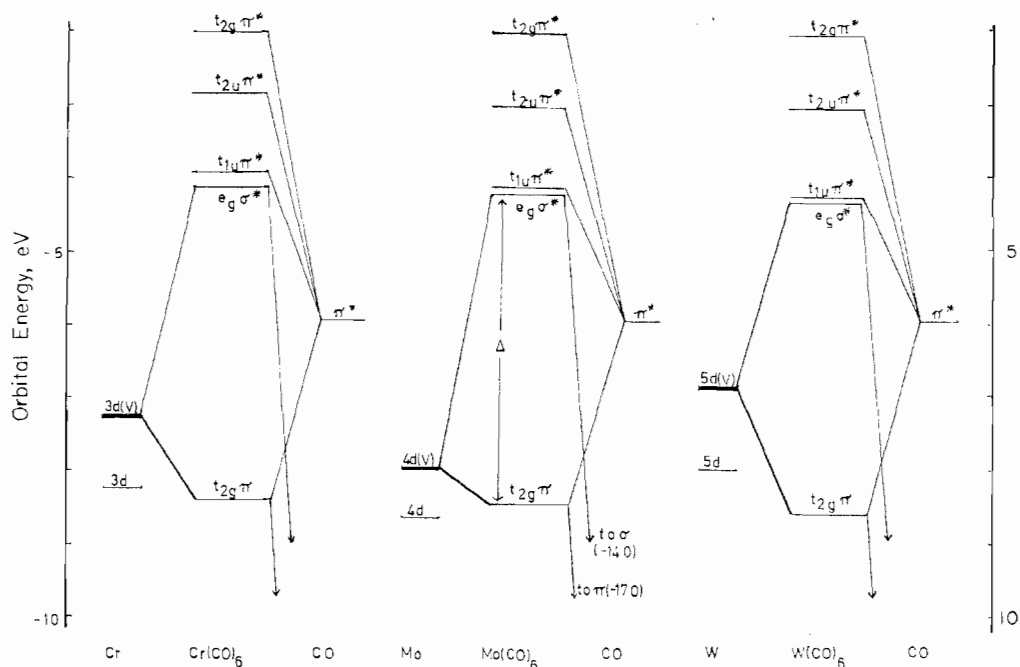


Figure 5.—The experimentally measured energy levels in the hexacarbonyls and their relation to the d-orbital levels in the free atoms and the π^* level in carbon monoxide. The levels marked 3d, etc., are energies for ionization transitions between lowest states of atom and ion, and the heavy lines marked 3d(V), etc., are valence orbital ionization potentials—see text.

sponds to an mo energy difference; *i.e.*, electron repulsion integrals have been ignored.

Previous discussions^{2,3,6} of the experimentally observed ionization potentials have attempted to compare these values with the first ionization potential for the metal atom. There are serious objections to such a comparison, apart from the difficulty of knowing whether a particular electron impact value is related to the adiabatic or to the vertical IP. First, the ionic and atomic ground terms²⁴ for tungsten, 6D and 5D , are different from those for the other two metals, 6S and 7S ; *i.e.*, for Cr and Mo the first IP refers to loss of an s electron from a d^5s configuration but for W the s electron is lost from a d^4s^2 configuration.

Second, while the atomic IP's refer to s-electron ionization, in the carbonyls the uppermost occupied orbital is of d type. Finally, even when the atomic IP's are adjusted, by means of the appropriate excitation energies,²⁴ to the values for d ionization, they still refer to transitions between ground terms, *i.e.*, to particular spin-orbit coupling configurations which are destroyed in the formation of a molecule. The appropriate atomic value for comparison with a molecular IP is an ionization between (hypothetical) space- and spin-randomized configurations of the atom and ion, *i.e.*, a valence orbital ionization potential (VOIP). Values of VOIP have been published^{25,26} for elements of the first transition series but not for the later series.

The left-hand side of each of the drawings in Figure 5 shows the atomic orbital IP for the lowest terms of d^5s ionization to d^4s and the heavy line for Cr is the

published VOIP assuming zero charge on the metal and ionization from d^5s . For W, several of the terms required to calculate a VOIP have not been observed, but an estimate has been made for the d orbitals by assuming that the missing terms of d^5s are distributed similarly to the Cr and Mo distributions. This W value and an averaged Mo value for d^5s are also shown as heavy lines. The right-hand sides of the drawings in Figure 5 show the energy calculated for the π^* orbital (5.95 eV) on the assumption that the first state A¹I of the CO molecule²⁷ arises from excitation of an electron in the σ nonbonding lone pair to the π^* orbital. Values for the vertical IP for the lower CO orbitals are from photoelectron spectroscopy.²⁸

It is clear from Figure 5 that the relative positions of the atomic ground-term d-orbital energies and the $2t_{2g}$ molecular levels do not correlate with the observed sequence of bonding characters. However, the differences between the estimated d VOIP's and the $2t_{2g}$ vertical IP's do fall in the sequence of bonding character, $Mo(CO)_6 < Cr(CO)_6 < W(CO)_6$, while the separation of d VOIP and CO π^* shows the opposite sequence.

The two factors which govern the interaction of two orbitals are²⁹ the separation of the orbital energies or diagonal elements of the energy matrix and the value of the off-diagonal element. In the Wolfsberg-Helmholtz approximation³⁰ the off-diagonal elements are set proportional to the overlap integrals, and it has been shown³¹ that, using fairly accurate wave functions,

(27) G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand and Co., Inc., New York, N. Y., pp 452, 520-522.

(28) D. W. Turner and D. P. May, *J. Chem. Phys.*, **45**, 471 (1966).

(29) *E.g.*, ref 25, pp. 20-23.

(30) See references and criticism in R. F. Fenske, *Inorg. Chem.*, **4**, 33 (1965).

(31) D. A. Brown and N. J. Fitzpatrick, *J. Chem. Soc.*, **A**, 316 (1967).

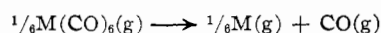
(25) C. J. Ballhausen and H. B. Gray, "Molecular Orbital Theory," W. A. Benjamin, Inc., New York, N. Y., 1965, pp 120-122.

(26) H. Basch, A. Viste, and H. B. Gray, *Theoret. Chim. Acta*, **3**, 458 (1965).

the d-p π overlaps for the three metals with a carbon atom are in the sequence Cr \approx W > Mo. Evidently from Figure 5 the energy separations are in the sequence Mo > Cr > W. Both factors combine to give a minimum bonding for molybdenum, and the energy separation, which is smallest for tungsten, presumably causes this element to have maximum π bonding. Although there are a number of uncertainties in this argument we suggest that the observed sequence of bonding characters may be rationalized in terms of the combined effects of d-p π overlap and the energy separation of the interacting orbitals.

The two other features worthy of note in Figure 5 are the very considerable raising of the CO π^* orbitals from their position in the isolated molecule and the approximate constancy of the molecular levels while the constituent atomic levels change considerably. The raising of the π orbitals may be connected with the back-donation,¹⁶ but it is not clear why the levels should be so similar in the three molecules.

The Thermodynamic Heats of Formation of the Hexacarbonyls.—The heats for the reactions



have been determined³² as $\Delta H = 1.18$ eV (Cr), 1.56 eV (Mo), and 1.83 eV (W), in apparent disagreement with the sequence of bonding characters deduced above. However, the strength of the binding is related to the heat of reaction of the metal and ligand in their (hypothetical) valence states rather than in their ground states (*cf.* the discussion in ref 20 and 32). Inspection of the observed terms²⁴ of d⁶, d⁸s, and d⁸p for chromium and molybdenum shows that the majority of Cr(I) terms have higher energy, referred to the ground state a⁷S, than the corresponding Mo(I) terms, so the promotion energy for chromium is probably greater than that for molybdenum. It is therefore possible that when the promotion energies are added to ΔH there will be an inversion of the relative positions of these two metals, so the sequence of ΔH is not necessarily inconsistent with the findings of the previous sections.

Bonding Considerations and Iron Pentacarbonyl.—Generally in the mononuclear carbonyls the filled orbitals fall into two groups. (Parts of the following discussion are to be found in ref 23 and 33.) The first group comprises the bonding and nonbonding orbitals which are mainly or entirely ligand in character, which will always accommodate as many electrons as are provided by the orbitals which are filled in the free carbon monoxide ligands; these orbitals are expected to have ionization potentials about as high as or higher than the IP³⁴ of the σ lone pair in carbon monoxide, 14.00 eV. The second group consists of orbitals which are mainly d in character, modified by σ -antibonding interactions and π interactions which may be metal-carbon bonding or antibonding, de-

pending upon whether the ligand π^* or π orbitals have the greater interaction. For there to be "back-bonding" in these compounds, as is suggested by a wide range of experimental evidence,²¹ the π^* interaction, which moves electrons from metal to ligand, must be greater than the π interaction, and in the following discussion we ignore the interaction with the π orbitals and refer to the π^* stabilization as " π bonding." The first IP of the molecule will involve loss of an electron from one of these latter orbitals, and to assign the IP it is therefore necessary to decide which of these orbitals is likely to be highest in energy and, if possible, what the likely energy separations are.

In the D_{3h} symmetry of iron pentacarbonyl the 3d orbitals transform as A₁', E', and E''. As a first approximation we neglect π bonding and consider only the σ -antibonding interactions. Under these conditions³⁵ the e'' (d_{zz}, d_{y²-z²}) orbitals are nonbonding, the e' (d_{x²-y²}, d_{xy}) and a₁ (d_{z²}) orbitals are antibonding as shown in Figure 6, and the eight valence electrons of iron(0) occupy the e'' and e' orbitals. (The δ , Δ notation follows ref 35.) It may readily be shown³⁶ that within the framework of the Wolfsberg-Helmholtz³⁰ approximation the rise in energy of such orbitals from the nonbonding zero (in this case e'') due to σ -antibonding effects is

$$\Delta E = \left(\frac{F^2}{4} \right) \frac{(H_{ii} + H_{jj})^2}{(H_{ii} - H_{jj})} G_{ij}^2 \quad (1)$$

where H_{ii} and H_{jj} are the diagonal elements in the orbital energy matrix for metal and ligand orbitals, usually approximated by a valence orbital ionization potential VOIP²⁵ and appropriate ligand IP, G_{ij} is the group overlap integral between the ligand group orbital and the metal orbital, and F is the proportionality factor between diagonal and off-diagonal elements. In any particular compound the ratios of energy raising may readily be calculated merely by evaluating the group overlap integrals in terms of two-atom overlap integrals, since the remaining terms are constant. Using a similar argument it has been shown³⁷ that if it is assumed that the equatorial and axial distances are the same, which seems³⁸ to be a very good approximation for Fe(CO)₅, then the ratio (δ/Δ) is 22/9. If the energy and two-atom overlap terms are kept constant and the symmetry is changed to octahedral, then Δ may be shown to be (3/8) Δ_0 , where Δ_0 is the octahedral splitting of t_{2g} and e_g orbitals. In the case of chromium hexacarbonyl Δ_0 is known²³ to be 35 kK or 4.35 eV. To use this value for a discussion of iron pentacarbonyl requires a knowledge of the energy terms and two-atom overlaps in eq 1. The ratio of overlaps for a carbon 2p σ orbital and chromium or iron d orbitals may be estimated as 1.1/1 from

(32) F. A. Cotton, A. K. Fischer, and G. Wilkinson, *J. Am. Chem. Soc.*, **81**, 800 (1959).

(33) W. F. Edgell, W. E. Wilson, and R. Summitt, *Spectrochim. Acta*, **19**, 863 (1963).

(34) D. W. Turner and D. P. May, *J. Chem. Phys.*, **45**, 471 (1966).

(35) R. F. W. Bader and A. D. Westland, *Can. J. Chem.*, **39**, 2306 (1961).

(36) See ref 25, p 137, problem 24.

(37) C. K. Jørgensen and H. H. Schmidtke, *Z. Physik. Chem. (Frankfurt)*, **38**, 118 (1963).

(38) M. I. Davis and H. P. Hanson, *J. Phys. Chem.*, **69**, 3405 (1965); *cf.* J. Donohue and A. Caron, *ibid.*, **70**, 603 (1966).

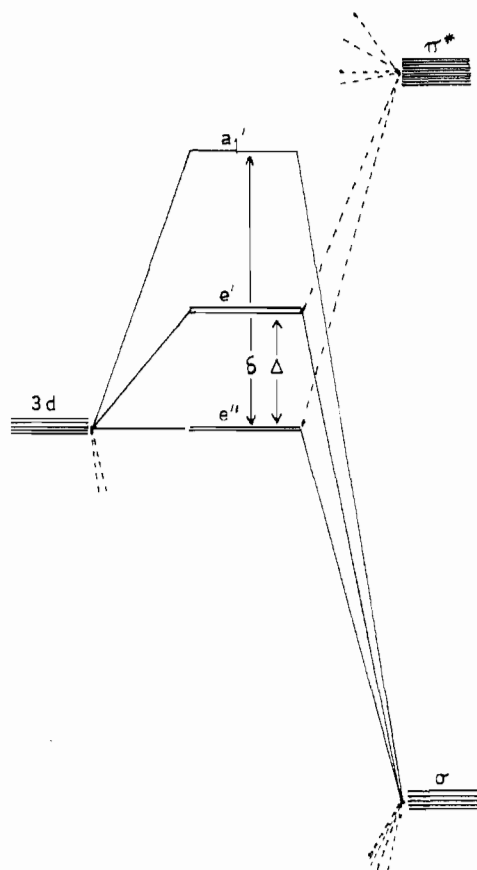


Figure 6.—The splitting of the d-type orbitals in D_{3h} symmetry by σ antibonding with five equidistant ligands.

published curves³⁹ for a metal-carbon distance of 2.1 Å, and the correction for the actual bond distance (1.8 Å) is negligible.³¹ However, the energy terms are sharply dependent upon charge and configuration of the metal atoms. Arbitrarily we assume zero metal charge and configuration $d^{n-1}s$, in which case the energy terms in (1) are approximately 280 kK for $\text{Cr}(\text{CO})_6$ and 340 kK for $\text{Fe}(\text{CO})_5$. Within the limits of these approximations the separation Δ of e' and e'' is calculated as 13 kK, 1.6 eV.

In addition to the σ -antibonding effects there will be additional effects from metal p-orbital mixing and π bonding. For the level of approximation used here p-d-orbital mixing is ignored because of the large energy gap²⁵ between the 3d and 4p orbitals of the iron atom. There is probably a large π -bonding contribution to the large Δ_0 in $\text{Cr}(\text{CO})_6$, but the effect of ignoring this is at least partially cancelled by the greater π bonding in the e'' orbitals in $\text{Fe}(\text{CO})_5$; evaluation of the forms of the group orbital overlaps (*cf.* ref 25, pp 111–117) shows that the π overlap for the e'' orbitals is 1.37 times larger than that for the e' orbitals. The predicted 1.6-eV separation of these orbitals agrees remarkably well with the 1.3-eV separation of the two peaks in the photoelectron spectrum, and accordingly these peaks are assigned to the e' and e'' d-type orbitals.

There are competing influences of σ antibonding

and π bonding upon the uppermost e' orbital. The photoionization curve rises very slowly, and there is a large difference between the adiabatic and vertical IP, so that the e' orbital has either strongly antibonding or strongly bonding character. For the orbital to have an over-all bonding character the π interaction would have to be much greater than the σ interaction, which seems unlikely since the π and σ overlaps, using accurate d wave functions, are very similar.^{31,39} We conclude that the e' orbital, though partially stabilized by π interactions, is antibonding in character. It was shown above that any π stabilization of the e'' orbitals would be greater than for the e' orbitals. Since the e'' orbitals have no σ interaction, any bonding character here is almost certainly one which stabilizes the molecule. Inspection of the photoelectron spectrum shows that the peaks corresponding to e' and e'' are both quite broad, considerably broader than the resolution half-width of the instrument, so it appears that the π -bonding character of the e' and e'' orbitals is approximately equal to the σ -antibonding character of the e' orbitals. This is another indication that there is strong back-donation of electrons from the metal to the ligand π^* orbitals.

The calculation of the separation of e' and e'' orbitals may be extended to give a calculated separation of e' and a_1' orbitals of 19 kK. The spectral transition ${}^1E'((e'')^4(e')^3(a_1')^1) \leftarrow {}^1A_1'((e'')^4(e')^4)$ is allowed in D_{3h} , but being mainly d-d in character it should not be very strong. The near-uv spectrum of $\text{Fe}(\text{CO})_5$ has been reported⁴⁰ as having intense absorption above 30 kK (shoulder at 36 kK ($\log \epsilon = 3.6$) and a peak at 41.6 kK ($\log \epsilon = 3.96$)) but with a weaker shoulder at 28.2 kK ($\log \epsilon = 2.27$). It seems not unreasonable to assign the 28.2 kK shoulder to the ${}^1E' \leftarrow {}^1A_1'$ absorption, and the more intense peaks to transitions to higher antibonding orbitals with more ligand character, so that the very crude calculation predicts the approximate region of the first transition. Though the excellent agreement of calculation and experiment on the $e'-e''$ separation is fortuitous, it does appear in these rough estimates that the energy separations are more strongly dependent on metal charge than on any other factor, so the assumed zero metal charge is probably quite close to the true charge.

Nickel Tetracarbonyl.—The expected splitting pattern of the d orbitals in T_d symmetry from σ -antibonding effects is one^{25,37} in which the t_2 (d_{xy} , d_{xz} , d_{yz}) orbitals are raised above the e ($d_{x^2-y^2}$, d_{z^2}) orbitals by $(4/9)\Delta_0$. Relating this to the chromium hexacarbonyl Δ_0 and applying the same type of correction for the change in overlaps and zero-charge metal orbital VOIP as in the previous section, the predicted tetrahedral energy difference Δ_t is 12 kK or 1.5 eV. Both t_2 and e orbitals may π bond to the ligand π^* orbitals, but the E group overlap is $\sqrt{3}$ times as great as the T_2 (d, π) group overlap,⁴¹ so the effect of π bonding, as with

(40) W. Hieber and D. Von Pigenot, *Chem. Ber.*, **89**, 193 (1956).

(41) See ref 20, pp 114–115 (we ignore ligand-ligand overlap); see also ref 5 in R. F. Fenske and C. C. Sweeney, *Inorg. Chem.*, **3**, 1105 (1964).

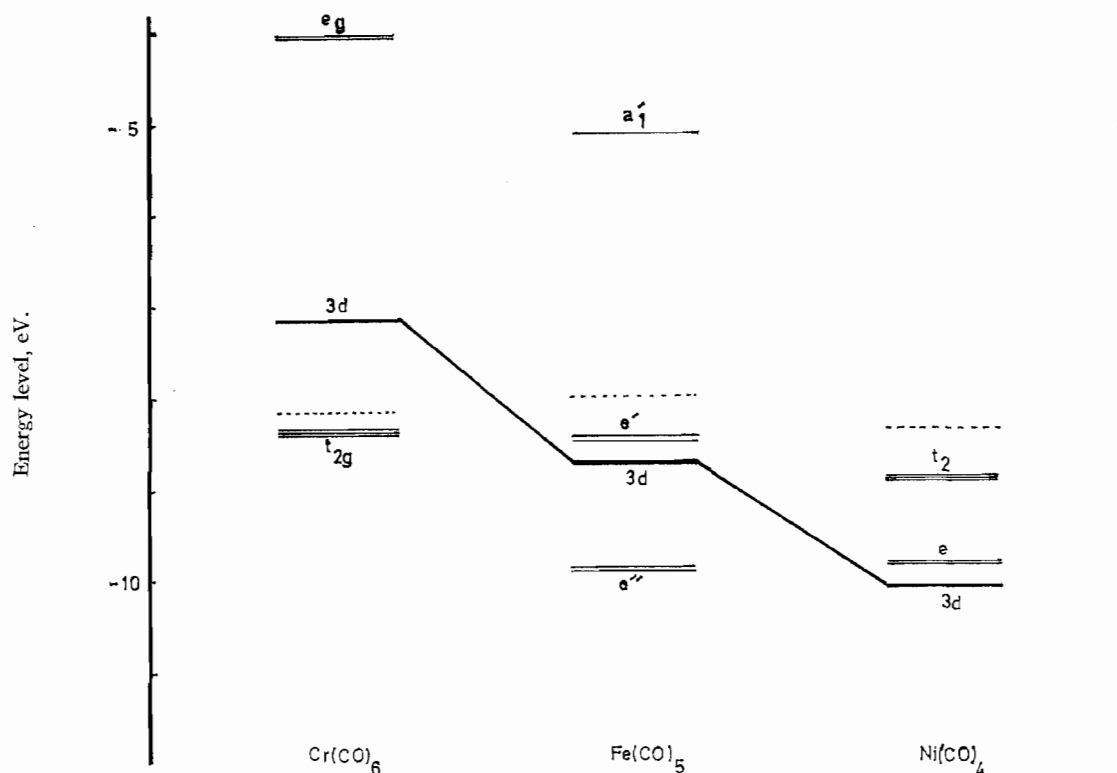


Figure 7.—The position of the d-type orbitals in the monomeric carbonyls determined from vertical ionization potentials and spectra and their relation to the d-orbital energies in the free atom (heavy lines). The dotted lines show the positions of the first adiabatic ionization potentials.

$\text{Fe}(\text{CO})_5$, is to increase any splitting due to σ -antibonding effects.

The ten valence electrons of $\text{Ni}(0)$ completely fill these five orbitals, so the first ionization will be from the t_2 orbitals, which are expected, extending the argument which was applied to $\text{Fe}(\text{CO})_5$, to be strongly antibonding. The experimental photoionization curve is in good agreement with this expectation, since it rises very slowly and there is a large difference of adiabatic and vertical IP. The calculated orbital separation here is somewhat larger than the observed separation of the peaks in the photoelectron spectrum, 0.8 eV, but this is not unreasonable considering the approximations involved, and the two peaks are therefore assigned to the t_2 and e orbitals. The relative intensities of the peaks correspond approximately with the degeneracies of these orbitals.¹⁷ The ion bond dissociation energy has been estimated as 0.75 ± 0.11 eV or 17 ± 3 kcal/mol. A recent investigation⁴² of the kinetics of C^{18}O exchange with nickel carbonyl gives an activation energy of 24.3 ± 0.4 kcal, which probably represents a dissociative process, but this is considerably more than our estimate of the bond-breaking energy in the ion. A possible explanation of the discrepancy is that the Jahn-Teller distortion of the $\text{Ni}(\text{CO})_4^+$ ion is so strong as to appreciably weaken the binding of one or more ligands; this is a common feature in the chemistry of the isoelectronic

divalent copper. Alternatively, the σ -antibonding character of the t_2 orbitals may increase upon ionization (*cf.* the hexacarbonyl discussion).

Comparison of d Orbitals in Chromium, Iron, and Nickel Carbonyls.—The observed ionization potentials and, for the first two compounds, the positions of the empty d-type orbitals deduced from spectra are plotted in Figure 7. The dotted lines show the position of the first adiabatic ionization potential, and the heavy lines are the metal d-orbital energies²⁵ (zero-charge VOIP for configuration d^n-1s). The most obvious feature is the almost constant value of the first adiabatic IP but it is difficult to give any analysis of this because the adiabatic value involves both ionization of the molecule and relaxation of the ion to a new equilibrium configuration. However, the first vertical IP's are almost constant, while the metal d-orbital energy decreases sharply as the atomic number increases. From the previous discussions it appears that the constancy is produced by a cancellation of effects. As the d-orbital energy decreases, the additional electrons are entering orbitals which are increasingly destabilized: the relatively high d-orbital energy of $\text{Cr}(0)$ is stabilized by π bonding in the t_{2g} orbitals; the much lower lying $\text{Ni}(0)$ d orbitals are destabilized by the σ -antibonding effect. The baricenter energy of the set of five d-type orbitals falls as atomic number increases and follows the free metal d-orbital energy very closely. We suggest that this also may be most easily explained by the assumption of a metal atom charge close to zero in all three compounds. Recent semi-

(42) J. P. Day, F. Basolo, R. G. Pearson, L. F. Kangas, and P. M. Henry, *J. Am. Chem. Soc.*, **90**, 1925 (1968).

empirical calculations⁴³ suggest that there is π bonding of the type discussed here but that the metal p orbitals become more important in the iron and nickel compounds and that the metal atom charge changes from +0.63 in $\text{Cr}(\text{CO})_6$ to -0.735 in $\text{Ni}(\text{CO})_4$. This is perhaps rather more variation than might be expected from our observations, and also the separation of the uppermost sets of orbitals in $\text{Ni}(\text{CO})_4$ and $\text{Cr}(\text{CO})_6$ predicted by these calculations is much smaller than is observed by photoelectron spectroscopy (see also ref 17). Some SCF calculations⁴⁴ for $\text{Ni}(\text{CO})_4$ indicate a metal charge of -1.0, but these predict a much wider separation of the uppermost sets of orbitals than is observed and also predict that the sequence of the top two orbital energies is $t_1 > e$, which is not in accord with the intensities of the bands shown in Figure 4.

Cobalt Nitrosyl Tricarbonyl.—This molecule, iso-electronic with nickel carbonyl, has C_{3v} symmetry.⁴⁵ From the group correlation tables,⁴⁶ the t_2 orbitals of T_d symmetry will split into e and a_1 orbitals in C_{3v} , whereas the e orbitals remain doubly degenerate in the lower symmetry. The σ orbital of the NO group transforms as A_1 , and the NO π^* orbitals transform as E, while the σ orbitals and the π^* orbitals of CO transform as $A_1 + E$, $A_1 + E$, $A_2 + E$. The stabilizing influence of the NO π^* orbitals is therefore confined to the e orbitals. The energy of the π^* orbitals in NO is given by the vertical IP of the free ligand, which may be estimated from the photoelectron spectrum published by Turner and May²⁸ as 9.66 eV, and the adiabatic IP of carbon monoxide in the excited state which has one electron in the π^* orbital has been shown above to be 5.95 eV. The π^* orbital in nitric oxide is thus at least 3.7 eV more stable than that in carbon monoxide. Unless there is a large difference in the overlaps of the carbon monoxide and nitric oxide orbitals with the metal d orbitals, the nitric oxide orbitals will be much more effective than the carbon monoxide orbitals in π stabilization or back-bonding, so the e orbitals will be lower in energy than the a_1 orbital, which has only σ -antibonding interactions with nitric oxide. The uppermost orbital in cobalt nitrosyl tricarbonyl is thus predicted⁴⁷ to be a_1 (d_{z^2}), strongly antibonding. The shape of the observed photoionization curve, very similar to that of nickel carbonyl, is in agreement with the prediction of a strongly antibonding orbital. It seems probable that fragmentation of the ion occurs before the e ionization can be observed. We have no direct evidence for fragmentation, but the observed curve is so similar to that of nickel carbonyl that this seems a likely explanation of the second increase of slope on the ionization curve. An alternative explanation of the second rise would be that this was due to

ionization from the e orbitals, but since these should be less antibonding than the a_1 orbital, a fairly well-defined ionization step would be expected rather than the continuously increasing rate of rise.

The vertical IP is very similar to that of nickel carbonyl and probably slightly greater. At first sight this is surprising since the d-orbital ionization energy of Co(0) is about 0.7 eV less than that of Ni(0). However, another difference between the two compounds is that the t_2 orbital in nickel carbonyl is antibonding from four carbon monoxide lone-pair interactions while the a_1 orbital is antibonding from three carbon monoxide and one nitric oxide lone-pair interactions. The vertical IP's for these σ orbitals in the free ligands²⁸ are 14.00 eV for CO and 16.52 eV for NO; *i.e.*, the lone pair in nitric oxide is 2.5 eV further away in energy from the metal d orbitals than the lone pair in carbon monoxide. Consequently the a_1 orbital will probably be less destabilized by the σ -antibonding effects than the t_2 in nickel carbonyl, and the constancy of IP may be the result of a cancellation between a rise in d-orbital energy and less antibonding effect.

An alternative explanation of the similarity in IP for the nickel and cobalt compounds would be that the cobalt atom was slightly more positive than the nickel atom, since increasing positive charge increases orbital ionization energies. We cannot rule out this possibility, but the reverse, that nickel is more positive than cobalt in this pair of compounds, seems unlikely. This is interesting since a very commonly used valence-bond description⁴⁸ of the nitrosyl bonding employs canonical forms which place more negative charge upon the metal than in a corresponding carbonyl compound, and formally nitric oxide in these compounds is described as a "three-electron donor." However, this formal device must be very far from a true description of the electron density distribution. The d-orbital energy of cobalt (d^8 s VOIP) is about 9.4 eV, and the π^* energy of nitric oxide is very similar (9.55 eV) so any appreciable negative charge on cobalt will raise all the d orbitals above the π^* level.

A certain amount of electron transfer seems probable, however, since nitric oxide coordination decreases coordinated carbonyl force constants and increases metal-carbon force constants.^{46,49} From our fragmentation onset data, the bond energies for ion dissociation are 1.26 ± 0.13 eV for $\text{CoNO}(\text{CO})_3^+$ and 0.75 ± 0.11 eV for $\text{Ni}(\text{CO})_4^+$, which may also indicate a stronger metal-carbon bond in the nitrosyl. Since we think it unlikely that the cobalt atom in $\text{CoNO}(\text{CO})_3$ is less positive than the nickel atom in $\text{Ni}(\text{CO})_4$, we suggest that it would be more accurate to speak of electron transfer to the other ligands rather than to the metal. In molecular orbital terms, the coefficients of the carbon monoxide π^* ligand orbitals in the expressions for the forms of the "d-type" molecular orbitals will be greater in cobalt nitrosyl tricarbonyl than in nickel carbonyl.

(43) A. F. Schreiner and T. L. Brown, *J. Am. Chem. Soc.*, **90**, 3366 (1968).

(44) W. C. Nieuwpoort, *Philips Res. Rept., Suppl.*, **6** (1965).

(45) L. H. Jones, *J. Chem. Phys.*, **28**, 1215 (1958); R. S. McDowell, W. D. Horrocks, Jr., and J. T. Yates, *ibid.*, **34**, 530 (1961).

(46) E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw-Hill Book Co., Inc., New York, N. Y., 1955, p 340.

(47) Note that different systems of axes are used for describing atomic orbitals in T_d , C_{3v} , and C_{2v} . The T_d system is shown in ref 20, p 109; in C_{3v} the z axis is the C_3 axis, in C_{2v} the z axis is along the C_2 axis as in T_d , but the x and y axes are rotated 45° from their positions in T_d .

(48) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1967, p 450 ff; ref 21, p 748.

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Since the orbitals are probably mainly metal in character in the nickel compound, increasing the ligand character, and hence the charge on the ligands, increases the metal-carbon bonding character.

Iron Dinitrosyl Dicarbonyl.—This has C_{2v} symmetry, in which there are no orbital degeneracies. C_{2v} is a subgroup of T_d but not of C_{3v} so our analysis of orbital splittings is based on the analysis of nickel tetracarbonyl rather than the cobalt compound. From the group correlation tables,⁴⁶ in going from T_d to C_{2v} the T_2 representation splits into $A_1 + B_1 + B_2$ and E splits into $A_1 + A_2$. The exact sequence of the "d-type" orbitals is not easy to decide generally, but if the deviation from tetrahedral symmetry is not too great, then the problem may be resolved into the sequence of orbitals which are derived from the t_2 orbitals, *i.e.*, a_1 ($d_{x^2-y^2}$), b_1 (d_{z^2}), and b_2 (d_{yz}). Consideration of the group overlaps for the σ and π interactions with CO and NO shows that the least stabilized orbital must be a_1 .

Experimentally the ionization potentials in Table III are seen to be very similar to those of the cobalt and nickel compounds. The free iron atom has a d-orbital energy²⁵ some 1.35 eV above that of the nickel atom, so as in the previous section it seems that either the uppermost a_1 orbital in the nitrosyl compound is less antibonding than the t_2 orbitals in nickel carbonyl or that the central metal atom carries a higher positive charge in the nitrosyl compound. Again this is not consistent with the formal negative charge in the valence bond formulation. The errors in the bond energy determinations for the molecular ions are such that it is not possible to say whether or not the bond energy in $Fe(NO)_2(CO)_2^+$ (1.21 ± 0.21 eV) is less than in $CoNO(CO)_3^+$ (1.26 ± 0.13 eV), but it is unlikely to be much greater. It seems therefore that the introduction of a second NO group does not enhance the metal-carbon bond strengthening produced by introducing the first one, and this is consistent with the infrared evidence⁴⁹ on carbonyl stretching force constants in these compounds.

The Fine Structure in the Hexacarbonyl Spectra.—It has been assumed in the Results that the series of inflections on the first ionization step corresponds to excitation of a vibration of the molecular ion, probably corresponding to ν_7 of the molecule. An alternative possibility is that this structure is due to weak autoionization from molecular states in the ionization continuum, and though we think it less likely because of the regularity of the energy differences between inflections, we cannot exclude this explanation. If the spacing is vibrational, there is an apparent increase in frequency from ν_7 , just within the error limits. How-

ever, the simple bonding-antibonding arguments of the earlier sections cannot be applied to this vibration since in addition to M-C stretching and bending it includes contributions from C-O stretching. Removal of an electron from the $2t_{2g}$ orbital will increase the C-O stretching force constant and decrease the M-C stretching force constant, so it is not clear whether an increase or decrease in frequency is to be expected.

We have interpreted the second rise on the ionization curves as the onset of the decomposition of the molecular ions to the fragments $M(CO)_5^+$ and CO. The mechanism of the ion fragmentation is not clear, but the increase of total ionization cross section at the fragmentation onset is in accord with studies of carbon dioxide⁵⁰ and nitrogen dioxide⁵¹ by photoionization with mass analysis; in both cases there is no observable change in the parent ionization cross section as the fragment ion cross section increases. The structure we observe on this second rise may be rationalized as vibrational in nature if the decomposition time τ of the excited molecular ion is so long that $h\tau^{-1}$ is considerably less than the observed spacing between the steps of about 0.2 eV, *i.e.* $\tau \gg 10^{-18}$ sec, which seems quite reasonable. However 0.2 eV does not even approximately correspond with any of the observed fundamental vibrations of the molecules, so autoionization seems a likely alternative explanation. For a decomposition step there are two possibilities, either normal autoionization to give the molecular ion or dissociative ionization giving the fragment ion. We have no information to decide between these possibilities, and studies with mass analysis and photoelectron energy measurement at varying photon energy would be very valuable.

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