Electron Impact Studies of Manganese and Rhenium Pentacarbonyl Halides[1]

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Abstract: The energetics of the ionization and dissociation of manganese and rhenium pentacarbonyl halides are reported. The ionization potentials (eV) are: $Re(CO)_5Cl = 9.18$; $Re(CO)_5Br = 9.07$; $Re(CO)_5I = 8.64$; $Mn(CO)_5Cl = 9.12$; $Mn(CO)_5Br = 8.97$; and $Mn(CO)_5I = 8.55$. These values are shown to be related to the ionization potentials of Re and Mn and to the relative electron-donating abilities of the halogen ligands. Appearance potentials for fragment ions were measured and used to calculate average ionic bond dissociation energies. The Re–CO bond is shown to be much stronger than the Mn–CO bond. Within the halogen series for each metal atom, the energy requirements for rupture of a single metal–CO bond follow the trend IM–CO > BrM–CO > ClM–CO. These results correlate well with the relative kinetic reactivities of $M(CO)_5X$ compounds in reactions where M–CO bond rupture is rate determining. Similarities and significant differences in the mass spectra are briefly discussed.

A recent report by Foffani, *et al.*,[2] relates the ligand donor ability to the measured ionization potentials of transition metal carbonyl nitrosyl complexes. The ionization potentials of $Co(CO)_3NO$ and $Fe(CO)_2(NO)_2$ are significantly lowered when PCl_3 or $P(OEt)_3$ is substituted for one of the CO groups in each complex. The reduction in the ionization potential is attributed to the greater donor capacities of PCl_3 or $P(OEt)_3$ relative to CO. This donor ability through the σ bond between the metal atom and the ligand is related to the ionization potential of the ligand itself.

In this report the conclusions of Foffani, *et al.*,[2] are shown to be valid for the two series, $Mn(CO)_5X$ and $Re(CO)_5X$, where X = Cl, Br, or I. The effect of the central transition metal atom on the ionization potential is also considered. In the unsubstituted carbonyls $M(CO)_x$ (M = Ni, Fe, Cr, Mo, or W, and x = 4, 5, or 6), investigations[3-8] have shown that the ionization potentials of these compounds are more closely related to the ionization potentials of the metal atoms than the carbon monoxide ligands. For example, the ionization potential of CO is 14.1 eV, while the ionization potentials of all $M(CO)_x$ compounds are 8–9 eV compared to M atom ionization potentials of 7–8 eV. However, discrepancies exist when the trend of the ionization potentials of the metal carbonyls is compared with the trend of the ionization potentials of the metal atoms. In three early reports,[4,5,8] the expected variation is observed for the series $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$.[9] However, two recent reports[6,7] suggest that any trend in this series is within the experimental limits of reproducibility. Thus the exact influence of the metal atoms on the molecular ionization potentials is debatable. Additional results for other metal atom systems are desirable for clarification. These results are provided by the comparison of the known ionization potentials of Re and Mn atoms with the values reported here for the metal pentacarbonyl halide pairs, $Re(CO)_5Cl$ and $Mn(CO)_5Cl$, $Re(CO)_5Br$ and $Mn(CO)_5Br$, and $Re(CO)_5I$ and $Mn(CO)_5I$.

This report then considers the influence of both the ligands and the metal atom on the ionization potentials. Additional considerations are the mass spectral features, the bond energy measurements from appearance potential data, and the correlation between electron impact measurements and kinetic reactivities.

Experimental Section

Mass Spectrometer Sampling. Four different sampling procedures were employed.

1. **Heated Inlet.** An all-glass MicroTek universal heated inlet system was used. However, some thermal decomposition was detectable with all samples. The thermal stabilities were in the order Re > Mn and I > Br > Cl.

2. **Direct Insertion.** The high vapor pressure of $M(CO)_5X$ compounds limited the successful application of this sampling technique. Sample consumption and ion-source contamination were extensive. Fluctuations of the ion intensities appreciably affected the quality of the mass spectra and the appearance potential measurements.

3. **Cold Probe.** The probe used here was similar to that described by Haddon, *et al.*[10] This technique is not yet convenient to employ, and poor spectral reproducibility made it undesirable for accurate mass spectral and appearance potential measurements. However, the technique was employed to guarantee that thermal decomposition was not affecting the mass spectra[11] obtained by use of a modified direct insertion technique.

4. **Modified Direct Insertion.** A probe similar in design to that described by Shadoff and Westover[12] was used extensively for these studies. It was found advantageous to substitute Teflon for the metal ferrules normally used to provide the vacuum seal around the sample tube. Much less torque is required to seal the Teflon–metal surface, and sample changeover is accomplished easily and rapidly. All the $M(CO)_5X$ samples had sufficient vapor pressure at room temperature for obtaining the mass spectra. Under these temperature conditions, thermal decomposition is negligible provided the ion source is cool and the inside surfaces of the metal

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

[9] $Ni(CO)_4$ and $Fe(CO)_5$ do not follow the predicted trend. It seems necessary to restrict the exact influence of the effect to carbonyls within one group in the periodic table.

[10] W. F. Haddon, E. M. Chait, and F. W. McLafferty, *Anal. Chem.*, 38, 1968 (1966).

[11] H. J. Svec and G. A. Junk, unpublished work.

[12] L. A. Shadoff and L. B. Westover, *Anal. Chem.*, **39**, 1048 (1967).

Table I. Ionization Potentials (eV) of $M(CO)_5X$ Compounds and the M and X Atoms

Sample	IP	IP of X[a]	IP of M[a]
$Re(CO)_5I$	8.64 ± 0.03	10.4	7.87
$Re(CO)_5Br$	9.07 ± 0.02	11.8	7.87
$Re(CO)_5Cl$	9.18 ± 0.03	13.0	7.87
$Mn(CO)_5I$	8.55 ± 0.02	10.4	7.43
$Mn(CO)_5Br$	8.97 ± 0.03	11.8	7.43
$Mn(CO)_5Cl$	9.12 ± 0.08	13.0	7.43

[a] Taken from R. W. Kiser, "Tables of Ionization Potentials," TID-6142, U. S. Atomic Energy Commission, Office of Technical Information, June 1960.

Table II. Appearance Potentials (eV) of $[M(CO)_yX]^+$ and Selected $[M(CO)_y]^+$ Fragment Ions[a]

	$[M(CO)_4X]^+$	$[M(CO)_3X]^+$	$[M(CO)_2X]^+$	$[M(CO)X]^+$	$[MX]^+$	$[M(CO)_3]^+$	$[M(CO)]^+$	$[M]^+$
$Re(CO)_5I$	10.29	12.04	14.65	16.69	19.20	14.71	...	>23
$Mn(CO)_5I$	...	9.49	10.46	12.37[b]	14.0	12.13	14.4[b]	16.2
$Re(CO)_5Br$	10.50	11.97	15.02	16.94	19.51	15.51	...	>23
$Mn(CO)_5Br$	...	9.55	10.47	11.72	12.4	12.7[c]	15.13[b]	16.5
$Re(CO)_5Cl$	10.45	11.92	14.85	16.84	19.27	...	...	23.1
$Mn(CO)_5Cl$	...	...	10.6[b]	11.3[b]	13.8[b]	9.7[d]	12.1[d]	14.8[d]

[a] All values except those noted were obtained using Warren's[13] procedure. [b] Vanishing-current procedure used; see F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press, New York, N. Y., 1957, p 30. [c] Two breaks observed near threshold; lower value is 9.9 eV. [d] These values are distorted due to thermal decomposition in the ion source. True values are probably higher than those recorded here.

probe have not been contaminated by deposits from previously decomposed metal carbonyls.

Ionization and Appearance Potential Measurements. All the ionization and appearance potential measurements were obtained using Warren's[13] extrapolated difference technique for evaluation of the ionization efficiency curves. These curves were plotted using an automatic device[14] to reduce the time necessary for each measurement. With this device, a single complete curve (55–5 eV) is plotted in less than 2 min. Multiple partial curves within a few volts of onset may be accumulated in a matter of minutes. Reproducibility of measurements is of the order of ±0.03 eV for parent ions to ±0.2 eV for some of the bare metal fragment ions. Comparisons are made rapidly between various related compounds, thereby improving significantly the uncertainties in the measurements and increasing confidence in consistently reproduced small differences which can be statistically supported.

Results and Discussion

Ionization Potentials. The measured ionization potentials are tabulated in Table I. It is evident that the trend in the ionization potentials of the halogen ligands is reflected in the ionization potentials of the $M(CO)_5X$ compounds. Thus, the influence of the electron donor ability of the ligand[2] has been established for two series of three compounds. In each case the difference in the ionization potentials of the halogens is considerably attenuated. For instance, the difference in the ionization potential of Cl and Br, $\Delta IP(Cl - Br)$, is 1.2 eV while $\Delta IP[Re(CO)_5Cl - Re(CO)_5Br]$ is only 0.11 eV. Similar comparisons can be made for the remainder of the data in the table and those of Foffani, *et al.*,[2] for $Fe(NO)_2(CO)P(OEt)_3$ and $Co(NO)(CO)_2(PCl_3)$.

From these results one can predict that the exchange of a ligand in a metal carbonyl will cause a shift in the ionization potential by about 20% of the difference in the ionization potentials of the ligands exchanged.

When the metal atoms are interchanged, a trend parallel to the ligand effect is observed. The difference in the ionization potentials of Re and Mn is reflected in the ionization potential of the $M(CO)_5X$ compounds. Three series of two compounds, $M(CO)_5Cl$, $M(CO)_5Br$, and $M(CO)_5I$, can be compared on the basis of the data reported in Table I. The shift is again about 20% of the difference in the ionization potentials of exchanged metals. Thus, the ionization potential of a $M(CO)_5X$ compound is related to both the ionization potential of the metal atom and the halogen ligand. The ligand effect (donor ability across a σ bond) supports the conclusions of Foffani, *et al.*,[2] about the ionization and probable bonding in metal carbonyls. The parallel metal atom effect adds further support to these conclusions and is supplementary evidence for ionization associated primarily with a transition metal electronic orbital.[2–7,15] It seems probable that these observations are generally applicable to metal carbonyl derivatives.

Table III. Average Ionic Bond Energies (eV) for $[M(CO)_5X]^+$ Molecule Ions

	Substituents lost							
Sample	1CO	2CO	3CO	4CO	5CO	2CO + X	4CO + X	5CO + X
$Re(CO)_5Cl$	1.3	1.4	1.9	1.9	2.0	...	...	2.3
$Mn(CO)_5Cl$	...[a]	...	0.5	0.6	1.0[b]	...	...	1.0
$Re(CO)_5Br$	1.4	1.5	2.0	2.0	2.1	2.2	...	>2.4
$Mn(CO)_5Br$	...[a]	0.3	0.5	0.7	0.7	1.3	1.2	1.3
$Re(CO)_5I$	1.6	1.7	1.9	2.1	2.1	2.1	...	>2.4
$Mn(CO)_5I$	...[a]	0.5	0.6	1.0	1.1	1.2	1.2	1.3

[a] The $[Mn(CO)_4X]^+$ fragment ion is absent from the mass spectrum. [b] Questionable value due to experimental complications.

Appearance Potentials and Bond Energies. The appearance potentials (AP) of most of the $[M(CO)_yX]^+$ fragment ions were measured. These values are listed in Table II. Previous results for monometal carbonyls[6,7] have shown that the average ionic bond energies calculated from appearance potential data are equal to the average neutral energies within 0.3 eV. If this is also true for these halogen derivatives, conclusions based on the results for ionic bond energies may be extended to the neutral bond energies. The average bond energies (BE) are calculated from the ionization potentials given in Table I, the appearance potentials given in Table II, and the equation

$$\text{Av ionic BE} = \frac{\text{AP of } [M(CO)_yX]^+ - \text{IP of } M(CO)_5X}{(5 - y)} \approx \text{av neutral BE} \quad (1)$$

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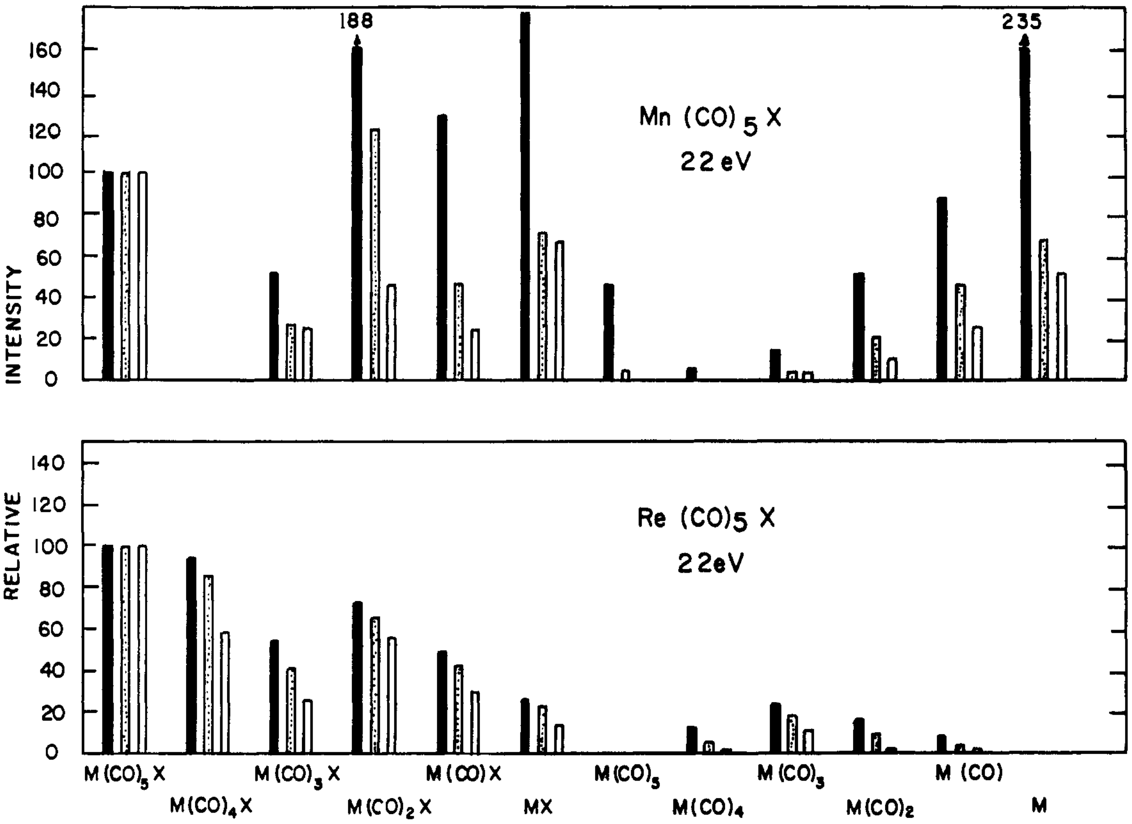

Figure 1. Parent ion normalized mass spectra (22 eV) of Mn$(CO)_5X$ and Re$(CO)_5X$ samples: solid bar, X = Cl; shaded bar, X = Br; open bar, X = I.

These values are tabulated in Table III. Inspection of these results leads to interesting conclusions about relative bond strengths in $M(CO)_5X$ compounds. First, the Re–CO bonds are much stronger than the Mn–CO bonds. Second, the first two M–CO bonds are weaker than the last three. Third, the energetics for loss of the first and second CO groups follow the trend, $M(CO)_5I > M(CO)_5Br > M(CO)_5Cl$. Fourth, no consistent halogen effect is observed for the average M–CO bond energy for rupture of three, four, or five CO groups.

The first and third conclusions given above may be used to qualitatively predict the kinetic reactivities of $M(CO)_5X$ compounds when SN1 mechanisms are involved. All other factors being equal, the trend in the rates of SN1 mechanistic reactions should be inversely proportional to the M–CO bond energy. The rate predictions based on mass spectrometric bond energy measurements for $M(CO)_5X$ compounds are Cl > Br > I and Mn > Re. Kinetic results for formation of *cis*-$M(CO)_4(L)X$ compounds by reaction of $M(CO)_5X$ with phosphines, phosphites, and other ligands[16,17] confirm these predictions. This correlation of mass spectrometric data with kinetic results may be indicative of more extensive relationships.

Mass Spectra. The 70-eV mass spectra of all of these $M(CO)_5X$ compounds, except $Re(CO)_5Br$, have been previously reported.[18,19] Our 70-eV mass spectra do not significantly differ. We have also measured the mass spectra of these compounds at low electron energy. Line diagrams of these results are shown in Figure 1 to focus the gross similarities and differences. The mass spectra of the three $Re(CO)_5X$ samples are very similar. Change in the halogen ligand exerts no significant influence on the fragmentation pattern. The same is true, although to a lesser degree, for the $Mn(CO)_5X$ compounds. In all six compounds, there is a fairly strong tendency to retain the halogen ligand. Regarding differences in the spectra, the manganese compounds exhibit increased fragmentation and a greater tendency to rupture the halogen ligand. The most notable, and unexpected, difference is the complete absence of a peak due to loss of a single CO group in the three manganese spectra while the analogous $[Re(CO)_4X]^+$ fragment ions cause intense peaks in all the rhenium spectra. This may be indicative of a significant difference in bonding and structure for these compounds.

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