Without a more detailed knowledge of the force fields which produce the distortion, it is difficult to interpret the above result.

4. Scalar Nuclear Coupling

The scalar nuclear spin–spin coupling has been neglected in the preceding analysis. In a complete analysis, only the most intense line pair (S_3 or R_3, Table I) is dependent on this parameter. Since the structure is very close to a square, and since the dependence on J_{ij} of the lines in the pair S_3 is much simpler than in the pair R_3, only S_3 will be considered. When scalar coupling is included in the spin Hamiltonian the line pair, S_3, is actually two pairs of lines, the separation between the lines in the two pairs (on the same side of the center of symmetry) being given by

$$\frac{1}{2}(\Delta S_{3a} - \Delta S_{3b}) = 3J_{12} = 3J_{\text{ortho}} \quad \text{(cps)}$$

where ΔS_{3a} and ΔS_{3b} would be the splittings between the two pairs of lines if they could be resolved. Again, since the most intense lines appear to be singlets (see Figure 2), it is only possible to put a limiting value on their separation (without resolution), and hence on J_{ortho}. Using computer simulation (see section 3b), this was estimated to be 4.0 cps, so that $3J_{\text{ortho}} \leq 4.0$ cps and $J_{\text{ortho}} \leq 1.3$ cps. Because of line-width effects (see preceding section), it is likely that J_{ortho} is even smaller. This result agrees with experimental observations by Pettit[7] in the nmr spectrum of a derivative of CIT, in which $J_{\text{ortho}} = 0.0$ cps.

5. Proton Chemical Shift Anisotropy

The center of the nematic spectrum is 10.8 cps downfield from the isotropic spectrum. In order to estimate the proton chemical shift anisotropy, S_{33} must be known. A value for S_{33} can be calculated by the following procedure: (1) the observed splittings are matched to the theoretical square (see Table Ia) splittings to yield S_{33}/R^3 (this is reasonable since the observed spectrum is very close to that predicted for a square; see section 3a); (2) using C–C and C–H bond lengths of 1.4 and 1.1 A, respectively, and assuming coplanarity of the carbon and hydrogen skeletons, the interproton distance, R, is found to be 2.96 A. S_{33} then equals ±0.02. Using this value for S_{33}, a chemical shift anisotropy of ±13 ppm is obtained. This is relatively large, being about the magnitude of shift anisotropies observed for acetylenic protons.[8]

Acknowledgment. The authors are grateful to Professor R. Pettit for supplying the cyclobutadiene compound.

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(8) A. Saupe and G. Englert, *Mol. Crystals*, **1**, 503 (1966).

Energetics of the Ionization and Dissociation of $Mn_2(CO)_{10}$, $Re_2(CO)_{10}$, and $ReMn(CO)_{10}$[1]

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Contribution from the Institute for Atomic Research and Department of Chemistry, Iowa State University, Ames, Iowa. *Received November 5, 1966*

Abstract: The mass spectra of $Re_2(CO)_{10}$, $Mn_2(CO)_{10}$, and $ReMn(CO)_{10}$ have been established and compared with the mass spectra of the monometal carbonyls. The electron-impact ionization potentials and the appearance potentials of the major fragment ions have been measured. These data are used to calculate specific and average bond dissociation energies for the ions. Metal–CO bond energies for $Re_2(CO)_{10}{}^+$ are shown to be greater than those of $Mn_2(CO)_{10}{}^+$. Metal–CO bond energies for $ReMn–(CO)_{10}{}^+$ are related to those observed for the Re_2 and Mn_2 compounds. A similar relative scale is predicted for the metal–CO bond energies of the neutral molecules. The calculated metal–metal dissociation energies (ev) of the neutral decacarbonyls and their ions to produce $\cdot M(CO)_5$ and $M(CO)_5{}^+$ are: Mn–Mn, 0.96, and [Mn–Mn]$^+$, 0.82; Re–Re, 2.22, and [Re–Re]$^+$, 2.08; Re–Mn, 2.67, and [Re–Mn]$^+$, 2.65. The ionization and dissociation mechanisms are discussed in terms of "isolated ionization" at one of the metal atoms in a dimetal carbonyl, and this model is tested by experimental observations.

Mass spectrometric studies of polynuclear carbonyls[2,3] and derivatives[4a] have been published recently. King[2] has worked primarily with the tri- and tetrametal carbonyls, while Preston and Reed[4a] and Lewis *et al.*,[4b] have concentrated their activities on the derivatives of dimetal carbonyls. No ionization and appearance potential measurements are reported by these authors. Winter and Kiser[3] report the ionization potentials of $Mn_2(CO)_{10}$ and $Co_2(CO)_8$, and the appearance potentials of some fragment ions from these materials are used to calculate ΔH_f(ion) values. Fragmentation patterns are also reported. These mass spectral patterns are important for the relationships to the quasi-equilibrium theory[5] and for structural information.[2] However, the energetics of the various fragmentations are also of fundamental importance.

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(1) Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission. Contribution No. 1979.

(2) R. B. King, *J. Am. Chem. Soc.*, **88**, 2075 (1966).

(3) R. E. Winters and R. W. Kiser, *J. Phys. Chem.*, **69**, 1618 (1965).

(4) (a) F. J. Preston and R. I. Reed, *Chem. Commun.*, 51 (1966); (b) J. Lewis, A. R. Manning, J. R. Miller, and J. M. Wilson, *J. Chem. Soc., Sect. A*, 1663 (1966).

(5) R. E. Winters and R. W. Kiser, *J. Chem. Phys.*, **44**, 1964 (1966).

Electron-impact studies may be used to gain an insight into the validity of the proposed bonding in the metal carbonyls. In addition, conclusions about structure, based on fragmentation pattern correlations, may sometimes be verified by appearance-potential measurements. Finally, bond dissociation energies which are of thermochemical interest are obtained from electron-impact data.

We have measured the energy required to produce fragment ions from the decacarbonyls of Re_2, Mn_2, and ReMn primarily to obtain bond dissociation energies and to study the mechanisms of ionization and dissociation. The strength of the metal–CO bonds and the metal–metal bonds reported here may not be absolutely accurate because of unknown kinetic and excitation energies. The possible errors due to these effects should be about equal for the series, $Mn_2(CO)_{10}$, $Re_2(CO)_{10}$, and $ReMn(CO)_{10}$. Thus, at least a good relative scale of bond energies is expected.

Experimental Section

Instrumentation. A General Electric mass spectrometer with modifications[6] previously described was used to obtain the data reported here. No additional modifications were required for this study.

Onset-Potential Measurements. The vanishing current[7] procedure was used to measure the onset potentials. Simultaneous sampling of the dimetal compounds and the xenon voltage calibrating gas was used.

Materials. The $Re_2(CO)_{10}$ and $Mn_2(CO)_{10}$ were purchased from Alfa Inorganics, Inc., and used without further purification. The pure sample of $ReMn(CO)_{10}$ was kindly furnished by Dr. H. D. Kaesz, University of California, Los Angeles, Calif.

Results and Discussion

Mass Spectra. Line diagrams of the 55-ev mass spectra are shown in Figure 1. Only the dimetal fragment ions are shown since these fragments cause most of the total ion current. The total intensity of the monometal ions is less than 20% of the total dimetal ion intensity for each sample. The ratios of these intensities are: $\Sigma Mn(CO)_x^+/\Sigma Mn_2(CO)_x^+ = 0.20$; $\Sigma Re(CO)_x^+/\Sigma Re_2(CO)_x^+ = 0.05$; and $[\Sigma Mn(CO)_x^+ + \Sigma Re(CO)_x^+]/ReMn(CO)_x^+ = 0.12$. The apparent preference for ruptures of the metal–CO bonds is a reflection of the lower strength of these bonds compared with the metal–metal bonds. The greater intensity of the monometal fragments for the manganese compound suggests that the metal–metal bond is weaker than the Re–Re bond. This conclusion based on the 55-ev mass spectra is supported by appearance-potential measurements discussed in the sections on dissociation energies. The enhanced tendency to form the higher mass fragments from $Re_2(CO)_{10}$ compared to $Mn_2(CO)_{10}$ follows the expected periodic trend in the metal–CO bond energies as the molecular weight increases within a transition metal group.

The numerical tabulation of Winters and Kiser[3] for $Mn_2(CO)_{10}$ has been converted to the per cent total ionization and is included as the broken bar graph in Figure 1. Their spectrum contains more of the lighter mass fragments, and this is probably due to a combination of sampling and instrumental factors.

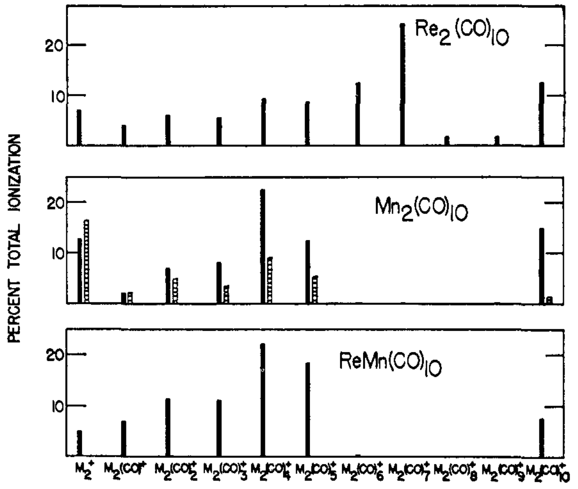

Figure 1. Mass spectra of dimetal decacarbonyls in per cent total ionization: solid bar, this report; broken bar, Winters and Kiser.[3]

The only ion currents observed here which are the result of metastable transitions are recorded in Table I. No attempt was made to observe other metastable ion currents by varying instrumental parameters such as sensitivity and repeller potential. Others undoubtedly exist, and the observation of these are important because they support the decomposition proposals[3,4b,5,8,9] of successive loss of CO groups in the unimolecular dissociation of metal carbonyls.

Table I. Observed Metastable Transitions

Process	Calcd *m/e*	Obsd *m/e*
$Mn_2(CO)_{10}^+ \rightarrow Mn(CO)_5^+ + Mn(CO)_5$	97.5	97.5
$Mn_2(CO)_4^+ \rightarrow Mn_2(CO)_3^+ + CO$	169.5	169.3
$Mn_2(CO)_5^+ \rightarrow Mn_2(CO)_4^+ + CO$	197.1	197.0

A possible rearrangement ion current was observed in the fragmentation of $ReMn(CO)_{10}$. Seven per cent of the total is due to a $[Re(CO)_6]^+$ ion current. Rearrangements involving migrations other than hydrogen are rare. Only one other such rearrangement, the OH group migration to form the *m/e* 46 ion current from amino acids,[10] has been positively confirmed at our laboratory. However, recent research reports from

Table II. Ionization Potentials of Dimetal Decacarbonyls

	Ionization potential, ev		
Sample	This report	Winters and Kiser[3]	Metal atoms
$Mn_2(CO)_{10}$	8.58	8.55	7.43
$Re_2(CO)_{10}$	8.27	...	7.87
$ReMn(CO)_{10}$	8.15	...	7.43, 7.87

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(6) G. A. Junk and H. J. Svec, *Anal. Chem.*, 37, 1629 (1965); Paper No. 84 presented at the Twelfth Annual Conference on Mass Spectrometry and Allied Topics, Montreal, June 1964.

(7) F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press Inc., New York, N. Y., 1957, p 30.

(8) An extensive report of observed metastable transitions of some monometal carbonyls has recently been published by R. W. Winters and J. H. Collins, *J. Phys. Chem.*, 70, 2057 (1966).

(9) B. Cantone, F. Grasso, and S. Pignataro, *J. Chem. Phys.*, **44**, 3115 (1966).

(10) G. A. Junk and H. J. Svec, *J. Am. Chem. Soc.*, **85**, 839 (1963).

Table III. Appearance Potentials and Heats of Formation of the $M_2(CO)_x{}^+$ Ions from $Mn_2(CO)_{10}$, $Re_2(CO)_{10}$, and $ReMn(CO)_{10}$

Ion	AP, ev[a]	Process	ΔH_f(ion), kcal/mole
Mn^+	22.13	$Mn_2(CO)_{10}$[b] $\rightarrow Mn^+ + Mn + 10(CO)$?	?
$Mn(CO)^+$	18.21	$\rightarrow Mn(CO)^+ + Mn + 9(CO)$	?
$Mn(CO)_2{}^+$	14.80	$\rightarrow Mn(CO)_2{}^+ + ?$	?
$Mn(CO)_5{}^+$	9.40	$\rightarrow Mn(CO)_5{}^+ + Mn(CO)_5$	?
$Mn_2{}^+$	18.73	$\rightarrow Mn_2{}^+ + 10(CO)$	309 (312)[c]
$Mn_2(CO)_2{}^+$	16.43	$\rightarrow Mn_2(CO)_2{}^+ + 8(CO)$	201
$Mn_2(CO)_3{}^+$	15.34	$\rightarrow Mn_2(CO)_3{}^+ + 7(CO)$	152
$Mn_2(CO)_4{}^+$	13.98	$\rightarrow Mn_2(CO)_4{}^+ + 6\ (CO)$	94 (95)
$Mn_2(CO)_5{}^+$	11.91	$\rightarrow Mn_2(CO)_5{}^+ + 5(CO)$	20 (37)
$Mn_2(CO)_{10}{}^+$	8.58	$\rightarrow Mn_2(CO)_{10}{}^+$	−188 (−189)
Re^+	37.55	$Re_2(CO)_{10}$[d] $\rightarrow Re^+ + ?$	?
$Re(CO)_5{}^+$	10.35	$\rightarrow Re(CO)_5{}^+ + Re(CO)_5$	. . .
$Re(CO)_4{}^+$	13.30	$\rightarrow Re(CO)_4{}^+ + ?$	?
$Re_2{}^+$	28.96	$\rightarrow Re_2{}^+ + 10(CO)$	319
$Re_2(CO)^+$	26.26	$\rightarrow Re_2(CO)^+ + 9(CO)$	231
$Re_2(CO)_2{}^+$	23.55	$\rightarrow Re_2(CO)_2{}^+ + 8(CO)$	142
$Re_2(CO)_3{}^+$	21.46	$\rightarrow Re_2(CO)_3{}^+ + 7(CO)$	67
$Re_2(CO)_4{}^+$	19.31	$\rightarrow Re_2(CO)_4{}^+ + 6(CO)$	−9
$Re_2(CO)_5{}^+$	16.71	$\rightarrow Re_2(CO)_5{}^+ + 5(CO)$	−95
$Re_2(CO)_6{}^+$	15.01	$\rightarrow Re_2(CO)_6{}^+ + 4(CO)$	−160
$Re_2(CO)_7{}^+$	13.55	$\rightarrow Re_2(CO)_7{}^+ + 3(CO)$	−220
$Re_2(CO)_8{}^+$	10.89	$\rightarrow Re_2(CO)_8{}^+ + 2(CO)$	−308
$Re_2(CO)_9{}^+$	9.57	$\rightarrow Re_2(CO)_9{}^+ + CO$	−365
$Re_2(CO)_{10}{}^+$	8.27	$\rightarrow Re_2(CO)_{10}{}^+$	−421
Mn^+	25.67	$ReMn(CO)_{10}$[e] $\rightarrow Mn + ?$	?
Re^+	30.93	$\rightarrow Re^+ + ?$	?
$Mn(CO)^+$	19.05	$\rightarrow Mn(CO)^+ + ?$	?
$Re(CO)_5{}^+$	10.80	$\rightarrow Re(CO)_5{}^+ + Mn(CO)_5$	. . .
$Re(CO)_6{}^+$	9.36	$\rightarrow Re(CO)_6{}^+ + Mn(CO)_4$ (?)	?
$ReMn^+$	25.98	$\rightarrow ReMn^+ + 10(CO)$	314
$ReMn(CO)^+$	23.00	$\rightarrow ReMn(CO)^+ + 9(CO)$	219
$ReMn(CO)_2{}^+$	19.75	$\rightarrow ReMn(CO)_2{}^+ + 8(CO)$	118
$ReMn(CO)_3{}^+$	16.94	$\rightarrow ReMn(CO)_3{}^+ + 7(CO)$	26
$ReMn(CO)_4{}^+$	14.65	$\rightarrow ReMn(CO)_4{}^+ + 6(CO)$	−53
$ReMn(CO)_5{}^+$	12.12	$\rightarrow ReMn(CO)_5{}^+ + 5(CO)$	−137
$ReMn(CO)_{10}{}^+$	8.16	$\rightarrow ReMn(CO)_{10}{}^+$	−360

[a] Reproducibility of all AP values reported here are from ±0.05 to 0.2 ev. [b] $\Delta H_f{}^\circ$ of $Mn_2(CO)_{10} = -385.9$ kcal/mole from calorimetric measurements: F. A. Cotton and K. R. Mouchamp, *J. Chem. Soc.*, 533 (1960). [c] Values calculated from Winters and Kiser data.[3] [d] $\Delta H_f{}^\circ$ of $Re_2(CO)_{10} \approx -611$ kcal/mole from AP data. No calorimetric value available. [e] $\Delta H_f{}^\circ$ of $ReMn(CO)_{10} \approx -548$ kcal/mole from AP data. No calorimetric value available.

Stanford[11] suggest that migration of bulky groups may occur more frequently than previously suspected. The absence of a comparable rearrangement ion current (if indeed the observed ion current is the result of a rearrangement process) due to a $M(CO)_6{}^+$ fragment in the mass spectrum of either $Mn_2(CO)_{10}$ or $Re_2(CO)_{10}$ suggests that the structure of $ReMn(CO)_{10}$ may be considerably different in the spatial configuration of the CO groups.

Ionization Potentials. The ionization potentials are recorded in Table II. Our value for $Mn_2(CO)_{10}$ is in excellent agreement with the value reported by Winters and Kiser.[3] The ionization potentials of the metal atoms are listed in column 4 for comparison. Since the CO ionization potential is about 14.0 ev, it appears as if ionization of these metal carbonyls involves removal of one of the valence electrons from the metal atom.

Appearance Potentials. The appearance potentials for the major fragment ions are listed in column 2 of Table III. Values of ΔH_f(ion) are tabulated in column 4. For comparison, values calculated from the appearance-potential data of Winters and Kiser[3] are given in parentheses. The decomposition reactions for forming the various dimetal ions are uncomplicated, and the processes listed in column 3 are undoubtedly correct. However, the reactions for forming the monometal fragments are questionable due to at least two possible reaction paths. Hence, no ΔH_f(ion) values are recorded for these fragment ions. Calorimetric measurements on $Re_2(CO)_{10}$ and $ReMn(CO)_{10}$ have not yet been reported so $\Delta H_f{}^\circ$ values for these materials are not available. We have estimated some values (see Standard Heat of Formation section) and these are used in the calculation of the ΔH_f(ion) values given for the $Re_2(CO)_x{}^+$ and $ReMn(CO)_x{}^+$ fragment ions. The appearance potentials for the $M_2(CO)_x{}^+$ fragment ions listed in Table III are plotted on the energy diagrams shown in Figure 2. The higher energy required to form each successively lighter fragment ion is experimental confirmation for the proposed stepwise decomposition mechanism.

Standard Heat of Formation Calculations. The $\Delta H_f(Mn_2{}^+)_g$ listed in Table III is 309 kcal/mole or 13.43 ev. This value can be used to approximate values for $\Delta H_f(Re_2{}^+)_g$ and $\Delta H_f(ReMn^+)_g$ from the fragmentation of their respective decacarbonyls. The approximation is based on the 6.00-ev difference between the $\Delta H_f(Mn_2{}^+)_g = 13.43$ ev and the ionization potential of $Mn(g) = 7.43$ ev. The difference between the ionization potential of Re(g) and the $\Delta H_f(Re_2{}^+)_g$ is also assumed to be 6.00 ev. Since the ionization potential of Re(g) is 7.87 ev, the value of $\Delta H_f(Re_2{}^+)_g$ is estimated to be 13.87 ev. The $\Delta H_f(ReMn^+)_g$ value is then in-

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(11) P. Brown and C. Djerassi, *J. Am. Chem. Soc.*, **88**, 2469 (1966), and references cited therein.

terpolated to be intermediate between the values of Re_2^+ and Mn_2^+ or 13.66 ev. These ΔH_f(ion) values and the appearance potentials of Re_2^+ and $ReMn^+$ are used in the equation

$$\Delta H_f(M_2^+)_g = AP(M_2^+) - 10[\Delta H_f^\circ(CO)] + \Delta H_f^\circ[M_2(CO)_{10}]_g \quad (1)$$

to calculate the standard heats of formation. The calculated values are −611 kcal/mole for $Re_2(CO)_{10}$ and −548 kcal/mole for $ReMn(CO)_{10}$. It is difficult to estimate the probable error in these values. In the interpolation to obtain the value for $\Delta H_f(Re_2^+)_g$, the heat of sublimation of Re and Mn are assumed to be equal. It is also assumed that the metal–metal bond strengths are equal. Both assumptions are erroneous since the ΔH_{subl} for Re and the bond energy of Re–Re are both greater than the corresponding values for Mn. However, in the process

$$2M(s) \longrightarrow M_2^+(g) + e \quad (2)$$

errors due to the assumptions tend to cancel one another. Since the bond-energy error is probably greatest, we consider these heat of formation values for $Re_2(CO)_{10}$ and $ReMn(CO)_{10}$ to be maximum (negative) values.

Metal–CO Dissociation Energies. The specific bond dissociation energies for the various ions have been calculated for the AP data and are listed in Table IV.

Table IV. Specific Bond Dissociation Energies of Ions

Dissociation process	Dissociation energy, ev Mn$_2$	Re$_2$	ReMn
$M_2(CO)_{10}^+ \rightarrow M_2(CO)_9^+$	0.7[a]	1.3	0.8[a]
$M_2(CO)_9^+ \rightarrow M_2(CO)_8^+$	0.7[a]	1.3	0.8[a]
$M_2(CO)_8^+ \rightarrow M_2(CO)_7^+$	0.7[a]	2.7	0.8[a]
$M_2(CO)_7^+ \rightarrow M_2(CO)_6^+$	0.7[a]	1.5	0.8[a]
$M_2(CO)_6^+ \rightarrow M_2(CO)_5^+$	0.7[a]	1.7	0.8[a]
$M_2(CO)_5^+ \rightarrow M_2(CO)_4^+$	2.1	2.6	2.5
$M_2(CO)_4^+ \rightarrow M_2(CO)_3^+$	1.4	2.2	2.3
$M_2(CO)_3^+ \rightarrow M_2(CO)_2^+$	1.0	2.1	2.8
$M_2(CO)_2^+ \rightarrow M_2(CO)^+$	1.2	2.7[b]	3.2
$M_2(CO)^+ \rightarrow M_2^+$	1.2	2.7[b]	3.0

[a] These are average values calculated from the dissociation of the first five CO groups. [b] These are average values calculated from the dissociation of the last two CO groups.

The almost equal energy required to dissociate the first five metal–CO bonds from $ReMn(CO)_{10}^+$ and $Mn_2(CO)_{10}^+$ suggests that these dissociations in $ReMn(CO)_{10}^+$ are due to Mn–CO bond ruptures. The near-equal energy required to dissociate the last five CO groups from $ReMn(CO)_{10}^+$ and $Re_2(CO)_{10}^+$ agrees with this suggested process. The negligible intensities of fragment ions between $M_2(CO)_{10}^+$ and $M_2(CO)_5^+$ (see Figure 1) for both the Mn_2 and ReMn decacarbonyls also support this proposal.

The average metal–CO bond dissociation energies from Table IV are

$$^1/_{10}[Mn_2(CO)_{10}]_g^+ \longrightarrow {}^1/_{10}Mn_2^+(g) + CO \quad \Delta H = 1.02 \text{ ev} \quad (3)$$

$$^1/_{10}[Re_2(CO)_{10}]_g^+ \longrightarrow {}^1/_{10}Re_2^+(g) + CO \quad \Delta H = 2.07 \text{ ev} \quad (4)$$

$$^1/_{10}[ReMn(CO)_{10}]_g^+ \longrightarrow {}^1/_{10}ReMn^+(g) + CO \quad \Delta H = 1.78 \text{ ev} \quad (5)$$

It is not possible to calculate the dissociation energies of the neutral molecules because of unknown ionization potentials and valence-state excitation energies for Re_2, Mn_2, and ReMn. However, it was shown for all the monometal carbonyls[12] that the bond dissociation energies of the ions are 0.3 to 0.5 ev per bond higher than the neutral dissociation energies. If this difference is true for the dimetal carbonyls, the neutral dissociation energies are 0.6, 1.7, and 1.4 ev per metal–CO bond in $Mn_2(CO)_{10}$, $Re_2(CO)_{10}$, and $ReMn(CO)_{10}$.

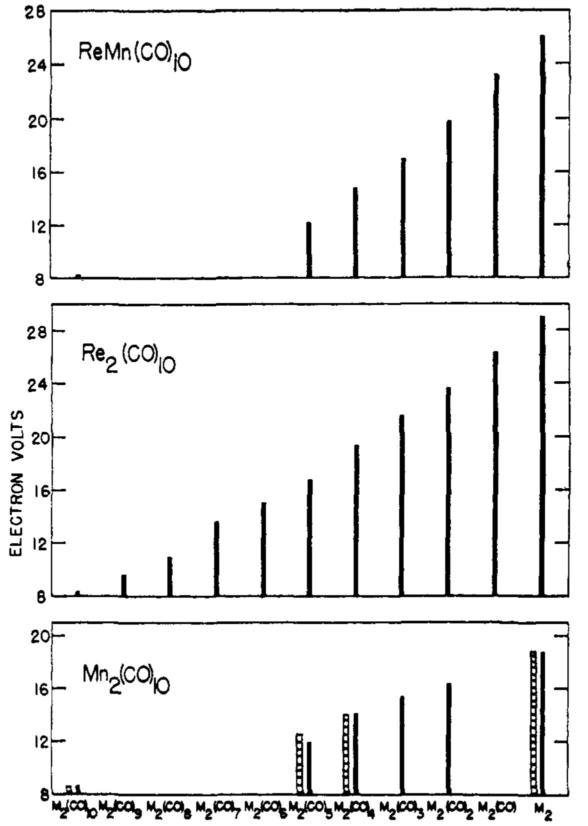

Figure 2. Appearance potentials of $M_2(CO)_x^+$ ions from $Mn_2(CO)_{10}$ $Re_2(CO)_{10}$, and $ReMn(CO)_{10}$: solid bar, this report; broken bar, Winters and Kiser.[3]

Metal–Metal Dissociation Energies. The ionization potential of the $\cdot M(CO)_5$ radical and the appearance potential of $M(CO)_5^+$ from $M_2(CO)_{10}$ are required to calculate the metal–metal dissociation energy of the decacarbonyls according to the equation

$$D[(CO)_5M\text{–}M(CO)_5] = AP[M(CO)_5^+] - IP[M(CO)_5] \quad (6)$$

Bidinosti and McIntyre[13] have recently measured the ionization potential of the $\cdot Mn(CO)_5$ radical and report a value of 8.44 ev, but no measurement of the ionization potential of the $\cdot Re(CO)_5$ radical is currently available. However, the difference in the ionization potentials of $\cdot Mn(CO)_5$ = 8.44 ev and $Mn_2(CO)_{10}$ = 8.58 ev is only 0.14 ev. We have assumed that this relationship is valid for $\cdot Re(CO)_5$ and $Re_2(CO)_{10}$, and the ionization potential of $\cdot Re(CO)_5$ is estimated to be 0.14 ev below the ionization potential of $Re_2(CO)_{10}$ (see Table II) or 8.13 ev. These values for the ionization potentials of $\cdot Mn(CO)_5$ and $\cdot Re(CO)_5$ radicals and the appearance potentials for $Re(CO)_5^+$ and $Mn(CO)_5^+$ (from Table I) were used in eq 6 to calculate the metal–metal dissociation energies listed in Table V. As expected, the Re–Re

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(12) Unpublished work from this laboratory.

(13) D. R. Bidinosti and N. S. McIntyre, *Chem. Commun.*, 555 (1966).

Table V. Metal–Metal Bond Dissociation Energies for $M_2(CO)_{10}$ (Ions and Neutral Molecules)

Process	ΔH, ev
$(CO)_5Mn\text{-}Mn(CO)_5 \rightarrow Mn(CO)_5 + Mn(CO)_5$	0.96[a]
$[(CO)_5Mn\text{-}Mn(CO)_5]^+ \rightarrow Mn(CO)_5 + Mn(CO)_5^+$	0.82
$(CO)_5Re\text{-}Re(CO)_5 \rightarrow Re(CO)_5 + Re(CO)_5$	2.22
$[(CO)_5Re\text{-}Re(CO)_5]^+ \rightarrow Re(CO)_5 + Re(CO)_5^+$	2.08
$(CO)_5Re\text{-}Mn(CO)_5 \rightarrow Re(CO)_5 + Mn(CO)_5$	2.67
$[(CO)_5Re\text{-}Mn(CO)_5]^+ \rightarrow Re(CO)_5^+ + Mn(CO)_5$	2.65
$[(CO)_5Re\text{-}Mn(CO)_5]^+ \rightarrow Re(CO)_5 + Mn(CO)_5^+$	. . .[b]

[a] This value compares favorably with the 0.82-ev value reported by Bidinosti and McIntyre[13] and is considerably lower than the 1.48-ev value calculated by Cotton and Mouchamp (see footnote *b* Table III) from calorimetric measurements. While the explanation for this discrepancy is not yet resolved, the relative scale of bond energies reported here should be reasonably accurate. [b] The low intensity of $Mn(CO)_5^+$ ion current made appearance-potential measurement unfeasible. For this reason no internal check on the ReMn dissociation energy calculated from this process was possible.

Table VI. Observed and Estimated Dissociation Energies of M–CO Bonds in Dimetal Decacarbonyls

Proposed process	Dissociation energy, ev Obsd av	 Estd av[a]
$(CO)_5Mn\text{-}Mn^+(CO)_5 \rightarrow Mn\text{-}Mn^+(CO)_5 + 5(CO)$	0.7	1.1[b]
$Mn\text{-}Mn^+(CO)_5 \rightarrow Mn\text{-}Mn^+ + 5(CO)$	1.4	1.4[c]
$(CO)_5Re\text{-}Re^+(CO)_5 \rightarrow Re\text{-}Re^+(CO)_5 + 5(CO)$	1.7	1.9[d]
$Re\text{-}Re^+(CO)_5 \rightarrow Re\text{-}Re^+ + 5(CO)$	2.5	2.3[e]
$(CO)_5Mn\text{-}Re^+(CO)_5 \rightarrow Mn\text{-}Re^+(CO)_5 + 5(CO)$	0.8	1.1[b]
$Mn\text{-}Re^+(CO)_5 \rightarrow Mn\text{-}Re^+ + 5(CO)$	2.7	2.3[e]

[a] Taken from unpublished data from this laboratory. [b] The ΔH for the process: $^1/_6Cr(CO)_6 \rightarrow {}^1/_6Cr + CO$. [c] The ΔH for the process: $^1/_6Cr^+(CO)_6 \rightarrow {}^1/_6Cr^+ + CO$. [d] The ΔH for the process: $^1/_6W(CO)_6 \rightarrow {}^1/_6W + CO$. [e] The ΔH for the process: $^1/_6W^+(CO)_6 \rightarrow {}^1/_6W^+ + CO$.

bond dissociation energy turns out to be greater than the Mn–Mn bond dissociation energy. The explanation for the even higher value for the bond energy of Re–Mn may be related to what was observed by Saalfeld and Svec[14] with the dihydride, $H_3Si\text{-}GeH_3$, in which overlap of vacant d orbitals in the mixed metal compounds tend to stabilize the metal–metal bond.[15] The difference in the electronegativities of Mn and Re may also contribute to the strength of the metal–metal bond in the mixed metal compound.

The metal–metal bond energy values of the ions follow the same trend as the neutral molecules, with the mixed compound having the highest value. Although the ions have less bond energy in each case, the difference is rather small indicating that charge has relatively little effect on the metal–metal bond.

Ionization and Dissociation Mechanism. It has been suggested that ionization of metal carbonyls[16] involves removal of one of the valence electrons from the metal atom. The highest probability for localization of the resultant positive charge from an "isolated ionization concept"[17] is therefore on the metal atom from which the electron is removed. To test this suggestion, the average dissociation energies of the metal–CO bonds from $M(CO)_6$, $M(CO)_6^+$, and $M_2(CO)_{10}^+$ have been investigated. These dissociation energies, calculated from the appearance-potential data in Tables III and IV and our studies of monometal carbonyls,[12] are listed in column 2 of Table VI. The estimated average dissociation energies are taken from chromium and tungsten hexacarbonyl data.[12] The average metal–CO bond dissociation energy for Cr–CO and Cr–CO$^+$ are taken to be roughly equal to that expected for Mn–CO and Mn–CO$^+$. The same approximation is made in the case of W and Re. The proposed bond ruptures are listed in column 1 of Table VI. No preferred charge localization exists between the metal atoms of the symmetrical carbonyls, and the choice listed is arbitrary. However, the charge is shown on the Re atom in the case of $ReMn(CO)_{10}$. The reason for this choice is the lower ionization potential observed for $Re_2(CO)_{10}$ compared with $Mn_2(CO)_{10}$ and the expectation that the lower energy process should occur preferentially. The agreement of the observed dissociation energies and the crudely estimated values suggests that the model proposed for ionization and dissociation is correct.

The almost equal average bond dissociation energy for the loss of the first five CO groups from $Mn_2(CO)_{10}$ (0.7 ev per bond) and $ReMn(CO)_{10}$ (0.8 ev per bond) supports this proposal, as does the close agreement of the dissociation of the last five CO groups from $Re_2(CO)_{10}$ (2.5 ev per bond) and $ReMn(CO)_{10}$ (2.7 ev per bond). Other observations which support this localized charge proposal are: the similarity of the mass spectra of $ReMn(CO)_{10}$ to $Mn_2(CO)_{10}$ from the parent ion to the $M_2(CO)_5^+$ ion; the similarity of the remainder of the spectrum of $ReMn(CO)_{10}$ to that observed for the $Re_2(CO)_5^+$ to Re_2^+ fragment ions from $Re_2(CO)_{10}$; and the high intensity of the $Re(CO)_5^+$ (100 units) relative to the $Mn(CO)_5^+$ (<1 unit). Thus, we conclude that the site of ionization of these complex molecules can be considered to be "isolated" and that low-energy processes are favored in the fragmentation; *i.e.*, the metal–CO bonds of the uncharged metal atom are the first to be ruptured. This observation is of fundamental mechanistic importance and should prove useful in future interpretations of the mass spectra of polymetal carbonyls and ligand-substituted metal carbonyls.

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