

Fe(CO)₄²⁻, *T_d*, 22321-35-3; Co(CO)₄⁻, *T_d*, 14971-27-8; Ni(CO)₄, *T_d*, 13463-39-3; Mn(CO)₄, *D_{4h}*, 71564-28-8; Mn(CO)₄⁻, *D_{4h}*, 71564-29-9; Fe(CO)₄, *D_{4h}*, 71564-30-2; Co(CO)₄⁺, *D_{4h}*, 71564-31-3; Fe(CO)₄⁻, *D_{4h}*, 71564-32-4; Co(CO)₄, *D_{4h}*, 71564-33-5; Fe(CO)₄²⁻, *D_{4h}*, 71564-34-6; Co(CO)₄⁻, *D_{4h}*, 71564-35-7; Ni(CO)₄, *D_{4h}*, 71564-36-8; Mn₂(CO)₁₀, 10170-69-1; Co₂(CO)₈, 10210-68-1; Fe₂H₂(CO)₈, 71500-60-2; Fe₃(CO)₁₂, 17685-52-8; HCo(CO)₄, 64519-62-6; HFe(CO)₄⁻, 18716-80-8; HMn(CO)₅, 16972-33-1; *cis*-H₂Fe(CO)₄, 22763-20-8; *trans*-H₂Fe(CO)₄, 71564-37-9; MnCl(CO)₅, 14100-30-2; MnBr(CO)₅, 14516-54-2; MnI(CO)₅, 14879-42-6; Mn(CH₃)(CO)₅, 13601-24-6; Mn(GeH₃)(CO)₅, 25069-08-3; Mn(SnH₃)(CO)₅, 71500-59-9; Mn(PH₃)(CO)₅, 71500-58-8; Mn(SH)(CO)₅, 59390-73-7; Mn(CH₃C≡O)(CO)₅, 13963-91-2; MnCl(CO)₄, 71518-81-5; MnBr(CO)₄, 71518-82-6; MnI(CO)₄, 71518-83-7; Mn(CH₃)(CO)₄, 71518-84-8; Mn(GeH₃)(CO)₄, 71518-85-9; Mn(SnH₃)(CO)₄, 71518-86-0; Mn(PH₃)(CO)₄, 71518-87-1; Mn(SH)(CO)₄, 71518-88-2; Mn(CH₃C≡O)(CO)₄, 71518-89-3; V(CO)₆, 14024-00-1; V(CO)₆⁻, 20644-87-5; Cr(CO)₆, 13007-92-6; Mn(CO)₆⁺, 21331-06-6.

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Application of Molecular Orbital Theory to Transition-Metal Complexes. 2. Calculation of Enthalpies of Activation for Dissociative Processes¹

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Molecular energies calculated with a modified extended Hückel theory are used to calculate enthalpies of activation and/or reaction for a number of dissociative processes involving transition metal carbonyl compounds. Metal-carbonyl, metal-hydride, and metal-metal bond dissociations are examined as well as the interaction of metal hydride with water to give $M^- + H_3O^+$. The effects of a series of ligands, X, on *cis* CO labilization in $MnX(CO)_5$, are examined and compared with similar calculations by other workers by use of the Fenske-Hall method.

Introduction

In the preceding paper,¹ we demonstrated that extended Hückel theory modified by the inclusion of two-body repulsion can successfully reproduce ground-state geometries, including bond lengths, for a number of transition metal carbonyl compounds. In principle, the molecular energies calculated therefrom may be compared to give internal energy (ΔE) of re-

action (or activation).² For example, for eq 1, ΔE can be calculated by adding the molecular energies of B and C (E_B and E_C) and subtracting that of A (E_A). The change in



$$\Delta E = E_B + E_C - E_A \quad (2)$$

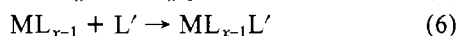
enthalpy (ΔH) is more commonly determined experimentally,

the relationship being as defined in eq 3. For solution chem-

$$\Delta H = \Delta E + \Delta(nRT) \quad (3)$$

istry under normal experimental conditions the term $\Delta(nRT)$ is usually relatively small (<1 kcal/mol) and so, for practical purposes, $\Delta H = \Delta E$. Therefore, throughout this paper we will refer to ΔH for simplicity in comparing calculated with experimental values. Under many circumstances, the enthalpy of activation is a more useful parameter. In theory this value may be found by carrying out the ΔH calculation for a large number of points along a reaction coordinate. The most positive ΔH would be the enthalpy of activation, that point representing the transition state of the reaction. However, this requires either knowing the reaction pathway or examining a number of possibilities to find the lowest energy pathway.

One of the simplest reactions to examine in this manner is the dissociative substitution of a metal complex as represented by eq 4-6.

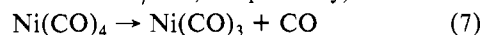


In this case, whereas the enthalpy of reaction (ΔH) would be that of eq 4, a similar calculation for eq 5 would approximate the enthalpy of activation (ΔH^\ddagger). Using the molecular energies calculated for the preceding paper¹ (summarized in Table I), we have computed the ΔH for a number of dissociative processes and compared them with experimentally determined values.

During the course of this study, Lichtenberger and Brown³ published an elegant molecular orbital study probing the reasons for the relative cis carbonyl labilization in $MnBr(CO)_5$ compared with $[Mn(CO)_6]^+$ and $MnH(CO)_5$. They used the nonempirical Fenske-Hall method⁴ and optimized the angular arrangement of ligands. Our calculations on similar complexes allow a comparison of these two widely different molecular orbital techniques with each other and with experimental evidence.

Results

A. M-CO Dissociation. The ΔH for the dissociation of one molecule of carbon monoxide from the parent carbonyl complexes can be calculated by adding and subtracting the energies of the proper optimized fragments (as found in Table I). As an example, a calculation based on eq 1 and 2 is given for $Ni(CO)_4$ in eq 7-9. The energy value used for carbon monoxide (178.29 eV) was obtained by optimizing the carbon-oxygen bond length and reproduces the experimental bond strength (255 and 256 kcal/mol,⁵ respectively).



$$\Delta H = (-639.15) + (-178.29) - (-818.42) \quad (8)$$

$$\Delta H = 0.98 \text{ eV} = 22.5 \text{ kcal/mol} \quad (9)$$

The calculated ΔH^\ddagger for $Ni(CO)_4$ agrees very well with the enthalpy of activation $\Delta H^\ddagger = 21$ kcal/mol, measured for the substitution by phosphorus donor ligands.⁶ There is, however, some concern that these are not simple dissociative reactions. While MEHT is unsuitable for comparing the molecular energies of $Fe(CO)_5$ and the spin unpaired fragment $[Fe(CO)_4]$,⁷ the calculated enthalpy of activation for carbonyl dissociation from $Fe(CO)_5$ with a spin-paired $[Fe(CO)_4]$ fragment compares favorably with kinetic measurements on the substitution of $Fe(CO)_4(PPh_3)$ ($\Delta H^\ddagger_{\text{calcd}} = 45.8$; $\Delta H^\ddagger_{\text{exptl}} = 42.5 \pm 1.2$ kcal/mol).⁸

For $Cr(CO)_6$, the calculated $\Delta H^\ddagger = 59$ kcal/mol is unreasonably high when compared with the reported value for carbonyl monoxide ($\Delta H^\ddagger = 39$ kcal/mol).⁹ Though the reason for this error is unknown, we have observed in many other calculations that MEHT disproportionately favors some of the

Table I. Calculated Molecular Energies

complex	symmetry	calcd energy, eV
$Ni(CO)_3$	D_{3h}	-639.15
$Ni(CO)_4$	T_d	-818.42
$Co(CO)_4^-$	T_d	-818.47
$Fe(CO)_4^{2-}$	T_d	-817.01
$Co(CO)_4$	D_{2d}, C_{3v}	-808.66
$Fe(CO)_4$	C_{2v}	-797.81
$Mn(CO)_4^+$	C_{2v}	-778.68
$Fe(CO)_5$	D_{3h}	-978.10
$Mn(CO)_5^-$	D_{3h}	-977.67
$Mn(CO)_5$	C_{4v}	-968.09
$Mn(CO)_5^+$	C_{4v}	-958.98
$Cr(CO)_5$	C_{4v}	-960.21
$Mn(CO)_6^+$	O_h	-1139.42
$Cr(CO)_6$	O_h	-1141.06
$CoH(CO)_3$	C_{3v}	-641.39
$CoH(CO)_4$	C_{3v}	-821.43
$FeH(CO)_4$	C_{2v}	-810.46
$FeH(CO)_4^-$	C_{3v}	-819.90
$FeH_2(CO)_4$	C_{2v}	-823.06
$MnH(CO)_4$	C_{2v}	-800.44
$MnCl(CO)_4$	C_{2v}	-905.52
$MnBr(CO)_4$	C_{2v}	-897.09
$MnI(CO)_4$	C_{2v}	-882.86
$Mn(SH)(CO)_4$	C_{2v}	-890.57
$Mn(PH_3)(CO)_4^+$	C_{2v}	-886.75
$Mn(CH_3)(CO)_4$	C_{2v}	-907.04
$Mn(GeH_3)(CO)_4$	C_{2v}	-892.53
$Mn(SnH_3)(CO)_4$	C_{2v}	-887.50
$Mn(CH_3CO)(CO)_4$	C_{2v}	-1086.24
$MnH(CO)_5$	C_{4v}	-980.90
$MnCl(CO)_5$	C_{4v}	-1085.56
$MnBr(CO)_5$	C_{4v}	-1077.17
$MnI(CO)_5$	C_{4v}	-1062.97
$Mn(SH)(CO)_5$	" C_{4v} "	-1070.61
$Mn(PH_3)(CO)_5^+$	" C_{4v} "	-1067.01
$Mn(CH_3)(CO)_5$	" C_{4v} "	-1087.25
$Mn(GeH_3)(CO)_5$	" C_{4v} "	-1072.95
$Mn(SnH_3)(CO)_5$	" C_{4v} "	-1067.90
$Mn(CH_3CO)(CO)_5$	" C_{4v} "	-1266.08
$Mn_2(CO)_{10}$	D_{4d}	-1937.90
$Co_2(CO)_8$	D_{3d}	-1618.97
$Fe_2H_2(CO)_8$	D_{2d}	-1621.35
$Fe_3(CO)_{12}$	D_{3h}	-2395.09

high symmetries with carbonyls trans to each other, e.g., species with D_{3h} or O_h symmetry, by some 10-20 kcal/mol over lower symmetry fragments. However, for related systems the errors are consistent, allowing us to deal with relative energies, as for the manganese derivatives described below.

It should be noted that while these ΔH values represent the energy necessary to break the metal-carbon bond they are not bond energies per se because they include a contribution from energy gained during fragment relaxation as carbon monoxide is lost. For example, carbonyl loss from $Ni(CO)_4$ without allowing the resulting fragment $[Ni(CO)_3]$ to relax to its optimum geometry gives rise to a $\Delta H^\ddagger = 33.6$ kcal/mol. Therefore relaxation of the $[Ni(CO)_3]$ fragment during the bond breaking process saves about 11 kcal/mol. In the iron and chromium cases about 9 and 1 kcal/mol, respectively, are gained by relaxation of the remaining fragment.

Mechanistic studies on $MX(CO)_5$ ($M = Mn, Re, Cr^-, W^-$) have established that some ligands, X, labilize the cis carbonyls, e.g., halogens, while others such as CO and PR_3 are less effective. Lichtenberger and Brown³ have reported an MO study of this system by using the nonempirical Fenske-Hall theory, which explains the experimental results. Our results, while qualitatively similar to theirs, more accurately reproduce the relative labilizing capabilities of a series of ligands. The calculated activation energies for various ligands are given in Table II, and a comparison with Lichtenberger and Brown's results is found in Table III.¹⁰ We find about 15 kcal/mol difference between the labilized species $Mn(CH_3CO)(CO)_5$

Table II. $\text{MnX}(\text{CO})_5 \rightarrow \text{MnX}(\text{CO})_4 + \text{CO}$

reaction no.	X	ΔH^\ddagger , kcal/mol			$\Delta\Delta H^a$ kcal/mol
		calcd	obsd	ref	
1	H	50.0			3.7
2	(CO) ⁺	49.4			3.1
3	GeH ₃	48.9	49.5	14	2.6
4	SnH ₃	48.6	41.4	14	2.3
5	(PH ₃) ⁺	47.0			0.7
6	CH ₃	44.2 (43.2) ^b	(32.5) ^c	13	-2.1
7	I	43.1	32.2	12	-3.2
8	Br	42.1	29.8	12	-4.2
9	Cl	41.8	27.5	12	-4.5
10	SH	40.2			-6.1
11	CH ₃ C(O)	35.5	27	11	-10.8
12	() ⁺	46.3			

^a $\Delta\Delta H$ = calculated ΔH^\ddagger minus ΔH^\ddagger of reaction 12 (no ligand).

^b Value in parentheses for *cis*- $\text{MnCH}_3(\text{CO})_4\text{PH}_3$. ^c Observed for *cis*- $\text{MnCH}_3(\text{CO})_4\text{P}(\text{CH}_2\text{C}_6\text{H}_5)_3$.

Table III. Comparison of MO Computational Technique

	MEHT, ^a kcal/mol	Fenske- Hall, ^b au ^c
$[\text{Mn}(\text{CO})_6]^+ \rightarrow [\text{Mn}(\text{CO})_5] + \text{CO}$ C_{4v}	49.5	1.07
$\text{MnH}(\text{CO})_5 \rightarrow \text{MnH}(\text{CO})_4 + \text{CO}$ C_{2v}	50.0	1.12
$\text{MnBr}(\text{CO})_5 \rightarrow \text{MnBr}(\text{CO})_4 + \text{CO}$		
C_{4v}	61.7	1.50
SBP-basal Br, $\theta = 90^\circ$ ^d	46.8	1.20
C_{2v}	41.2	0.92

^a This work. ^b Reference 3. ^c Atomic units. 1 au = 627 kcal/mol. ^d SBP = square-based pyramid.

and the parent complex $[\text{Mn}(\text{CO})_6]^+$ compared with the known experimental spread of about 15 kcal/mol between the former and $\text{Mn}(\text{SnPh}_3)(\text{CO})_5$.¹¹⁻¹⁴ The order of effectiveness of X toward *cis* labilization as reported by Atwood and Brown¹⁵ is, for the most part, reproduced by our calculations and decreases in the order $\text{CH}_3\text{C}(\text{O}) > \text{SH} > \text{Cl} > \text{Br} > \text{I} > \text{CH}_3 > (\text{PH}_3)^+ > \text{SnH}_3 > \text{GeH}_3 > (\text{CO})^+ > \text{H}$. The ordering is consistent with the reported experimental enthalpies of activation except that the positions of the germyl and stannyl ligands are reversed. The positions of the $(\text{PH}_3)^+$ and $(\text{CO})^+$ ligands are consistent with qualitative observations of their reactivity and are similarly placed in Atwood and Brown's series.¹⁵

The complex $\text{MnCH}_3(\text{CO})_5$ is known not to substitute by carbonyl dissociation but rather by methyl migration to form an acetyl complex which then decarbonylates, eq 10. $\text{Me-CH}_3\text{Mn}(\text{CO})_5 + \text{L} \rightarrow \text{CH}_3\text{COMn}(\text{CO})_4\text{L} \rightarrow \text{CH}_3\text{Mn}(\text{CO})_4\text{L} + \text{CO}$ (10)

Measurements for both steps in the case where $\text{L} = \text{CO}$ have been obtained by Calderazzo and Cotton¹¹ and are $\Delta H^\ddagger = 14$ and 27 kcal/mol, respectively. If the calculated relationship between iodine and methyl is to be trusted, carbonyl dissociation from $\text{MnCH}_3(\text{CO})_5$ would require $\Delta H^\ddagger = 33-34$ kcal/mol, thereby explaining the absence of a competitive dissociation at lower temperatures. Recent kinetic studies on the internal aromatic metalation of *cis*- $\text{MnCH}_3(\text{CO})_4\text{P}(\text{CH}_2\text{C}_6\text{H}_5)_3$ ¹³ have shown that in this case carbonyl dissociation is the rate-determining step ($\Delta H^\ddagger = 32.5$ kcal/mol). Calculations on *cis*- $\text{MnCH}_3(\text{CO})_4(\text{PH}_3)$ and its decarbonylation product give a ΔH^\ddagger lower than for the pentacarbonyl case (see value in parentheses—Table II) and very similar to $\text{MnI}(\text{CO})_5$. This labilization of $\text{MnX}(\text{CO})_4\text{L}$ compared to $\text{MnX}(\text{CO})_5$ has been demonstrated experimentally by Atwood and Brown for $\text{X} = \text{Br}$ and $\text{L} = \text{phosphines, amines, and phosphates}$.¹⁶ The reason for the lack of a competitive methyl migration reaction pathway for the *cis*- $\text{MnCH}_3(\text{CO})_4\text{L}$ is not clear.

A special note should be made of the calculated ΔH for carbonyl dissociation from $\text{MnH}(\text{CO})_5$. For some time, substitution of the hydride complex was assumed to occur by a dissociative mechanism by analogy with other $\text{MnX}(\text{CO})_5$ complexes, and thus hydride was considered to be a labilizing ligand. However, Byers and Brown¹⁷ have recently shown that substitution with $\text{MnH}(\text{CO})_5$ occurs by two mechanisms, one of which is radical in nature and the other proposed to involve hydride migration to a carbonyl giving a formyl complex intermediate. They do not suggest a competitive dissociative substitution pathway. Calculations support this, suggesting that a hydrido ligand is nonlabilizing.¹⁸

Atwood and Brown have proposed that the ability of X to labilize carbonyl loss depends on stabilization of the transition state relative to the ground state through π donation. A quantitative expression of this stabilization can be obtained by comparing ΔH for the reactions 11 and 12.

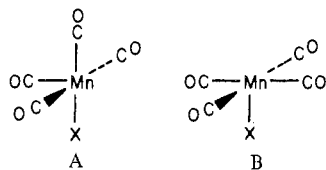


Let $\Delta\Delta H = \Delta H(11) - \Delta H(12)$. If $\Delta\Delta H$ is greater than zero, $\text{MnX}(\text{CO})_5$ is more stabilized by X than $[\text{MnX}(\text{CO})_4]$; the converse also holds. The same values for $\Delta\Delta H$ can be obtained by subtracting ΔH for reaction 12 of Table II from those for reactions 1 through 11 and the results are given in the last column of Table II. The known labilizing ligands, i.e., halogens, have negative values and hence stabilize the transition state that much more than the ground state. It is interesting that phosphine has the same effect as no ligand (reaction 5 vs. 12) while the methyl group is apparently a significant π donor.

Lichtenberger and Brown³ have pointed out that whereas the relative rates of CO loss vary in the order $\text{X} = \text{Cl} > \text{Br} > \text{I}$, the σ and π orbital energies vary in the order $\text{Cl} < \text{Br} < \text{I}$. The latter suggests that iodine should be a better π donor than bromine, etc. A comparison of the π overlap between the manganese d and the halogen p orbitals of the complexes $[\text{MnX}(\text{CO})_5]$ reveals that $\text{Cl} > \text{Br} > \text{I}$, strongly suggesting that the degree of overlap is more important than the orbital energies. This is consistent with photoelectron studies which indicate that the interaction of the halide orbitals with the metal in the ground state decreases in the order $\text{Cl} > \text{Br} > \text{I}$.¹⁹ Examination of the $[\text{Mn}(\text{PH}_3)(\text{CO})_5]^+$ case reveals that whereas the p-type orbitals of phosphine are energetically similar to the chlorine p orbitals, their overlap with manganese d orbitals is considerably reduced because of involvement in phosphorus-hydrogen bonding. This is consistent both with the classification of phosphines as poor π donors and with their relatively poor labilizing ability.

Comparing the calculated activation energies with experimental data shows that the former are consistently about 10 kcal/mol too high. Though some may consider this a large error, it is remarkably small for such an approximate MO theory. The real value of the technique is in the calculation of relative energies of similar systems as is shown by the data presented here.

To this point, the calculations described have not distinguished whether the carbonyl from $\text{MnX}(\text{CO})_5$ is *cis* or *trans* to X. We have shown only energy differences between optimized ground and intermediate states. One approach to determining which carbonyl is labilized is to simply remove either a *cis* or the *trans* carbonyl from the coordination sphere without letting the resulting intermediate relax to its optimum geometry. Calculating ΔH^\ddagger by using the "unrelaxed" fragments A and B, we find that the ejection of the *cis* carbonyl is favored over the *trans* carbonyl by 15 kcal/mol (46.8 kcal/mol vs. 61.7 kcal/mol). The difference between this *cis* CO ejection value and the one given in Table II (41.2 kcal/mol)



is due to the energy gained by relaxation of the intermediate to its optimum geometry. The optimized calculated manganese-carbon bond lengths of the ground state do reflect this difference; i.e., the trans Mn-C distances optimize 0.03–0.05 Å shorter than the cis Mn-C distances, suggesting that the latter bond is somewhat weaker. X-ray crystallographic data for $\text{MnCl}(\text{CO})_5$ show an even larger variation (0.07 Å).²⁰

B. M–H Dissociation. The energies calculated for homolytic cleavage of the M–H bond are between 60 and 70 kcal/mol, consistent with the best current estimates for the metal-hydrogen bond strength²¹ (Table IV, reactions 1–4).

C. M–M Dissociation. The energies calculated for metal-metal bond cleavage for four cases are given in Table IV (reactions 5–8). The results for Mn are in excellent agreement with the literature value of about 37 kcal/mol.²² Though the difference is small, it is reassuring to find the calculated energy of the Co–Co bond is less than that for the Mn–Mn bond, a value consistent with the relative ease of substitution of $\text{Co}_2(\text{CO})_8$ compared to $\text{Mn}_2(\text{CO})_{10}$. These reactions are known to take place by initial cleavage of the metal-metal bond.²³ Less is known about the reactivity of $\text{Fe}_2\text{H}_2(\text{CO})_8$; however, the relatively low calculated ΔH (10.5 kcal/mol) suggests a facile monomer-dimer equilibrium may be important. This is similar to $[\text{Fe}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_3]_2$ which has been experimentally determined at $\Delta H_{\text{dimerization}} = -13$ kcal/mol.²⁴ The calculation with $\text{Fe}_3(\text{CO})_{12}$ should be viewed with caution because we have used the low-spin $\text{Fe}(\text{CO})_4$ molecular energy value.⁷ We also have not explored the dissociation of $\text{Fe}_3(\text{CO})_{12}$ to give $\text{Fe}_2(\text{CO})_8$ and $\text{Fe}(\text{CO})_4$.

D. Enthalpies of Hydrogen Elimination from Metal Hydrides. The results from sections B and C (Table IV, reactions 1–8) and a knowledge of the strength of the H_2 bond (104.2 kcal/mol)²⁵ can be used to give the thermodynamic relationships found in the middle of Table IV (reactions 9–13). Qualitatively, the results for $\text{MnH}(\text{CO})_5$ and $\text{CoH}(\text{CO})_4$ are correct; when heated or photolyzed under H_2 , either dimer will form some hydride complex, but under ambient conditions the hydrides will spontaneously decompose to H_2 and the dimers.

$\text{FeH}_2(\text{CO})_4$ has been reported to decompose to H_2 and the dimer $\text{Fe}_2\text{H}_2(\text{CO})_8$ under reduced pressure.²⁶ On consideration of the positive ΔH calculated for this reaction, it would be interesting to check the stability of $\text{FeH}_2(\text{CO})_4$ under an atmosphere of hydrogen. It is also noteworthy that what might be expected to be the more likely decomposition pathway for $\text{FeH}_2(\text{CO})_4$ and conceptually simpler, i.e., reductive elimination of H_2 followed by clusterification of the resulting $[\text{Fe}(\text{C}-\text{O})_4]$ fragments to $\text{Fe}_3(\text{CO})_{12}$, is calculated to be thermodynamically less favorable and is, in fact, not observed in the laboratory.

E. Reaction of M–H + H_2O . MEHT may also be applied to intermolecular heterolytic cleavage of bonds. One of the simplest cases is the removal of a proton by water from a metal hydride. The energies of H_2O and H_3O^+ ²⁷ were therefore calculated, allowing the computation of the results shown in the latter part of Table IV (reactions 14–17). The values shown in parentheses are estimated from known $\text{p}K_a$ values.²⁶ Though the calculated ΔH values and the differences between them are incorrect, the relative ordering of the three neutral species is correct. That only the negatively charged $[\text{FeH}(\text{C}-\text{O})_4]^-$ is out of order (and has the wrong sign) is very encouraging and suggests that qualitative studies of ionic solution equilibria may be possible.

Table IV

no.	reaction	calcd ΔH , kcal/mol
1	$\text{CoH}(\text{CO})_4 \rightarrow \text{H}\cdot + \cdot\text{Co}(\text{CO})_4$	63.7
2	$\text{MnH}(\text{CO})_5 \rightarrow \text{H}\cdot + \cdot\text{Mn}(\text{CO})_4$	64.7
3	$\text{FeH}_2(\text{CO})_4 \rightarrow \text{H}\cdot + \cdot\text{FeH}(\text{CO})_4$	59.8
4	$\text{FeH}(\text{CO})_4 \rightarrow \text{H}\cdot + \text{Fe}(\text{CO})_4$	61.0 ^a
5	$\text{Mn}_2(\text{CO})_{10} \rightarrow 2\cdot\text{Mn}(\text{CO})_5$	39.6
6	$\text{Co}_2(\text{CO})_8 \rightarrow 2\cdot\text{Co}(\text{CO})_4$	38.0
7	$\text{Fe}_2\text{H}_2(\text{CO})_8 \rightarrow 2\cdot\text{FeH}(\text{CO})_4$	10.5
8	$\text{Fe}_3(\text{CO})_{12} \rightarrow 3\text{Fe}(\text{CO})_4$	38.2 ^a
9	$2\text{MnH}(\text{CO})_5 \rightarrow \text{H}_2 + \text{Mn}_2(\text{CO})_{10}$	-14.5
10	$2\text{CoH}(\text{CO})_4 \rightarrow \text{H}_2 + \text{Co}_2(\text{CO})_8$	-14.7
11	$2\text{FeH}_2(\text{CO})_4 \rightarrow \text{H}_2 + \text{Fe}_2\text{H}_2(\text{CO})_8$	+5.0
12	$\text{FeH}_2(\text{CO})_4 \rightarrow \text{H}_2 + \text{Fe}(\text{CO})_4$	+16.6 ^a
13	$3\text{FeH}_2(\text{CO})_4 \rightarrow 3\text{H}_2 + \text{Fe}_3(\text{CO})_{12}$	+11.5
14	$\text{CoH}(\text{CO})_4 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{Co}(\text{CO})_4^-$	-3.5 [<0] ^b
15	$\text{FeH}_2(\text{CO})_4 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{FeH}(\text{CO})_4^-$	1.2 [5.3]
16	$\text{MnH}(\text{CO})_5 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{Mn}(\text{CO})_5^-$	3.0 [9.3]
17	$\text{FeH}(\text{CO})_4^- + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{Fe}(\text{CO})_4^{2-}$	-5.5 [17.3]

^a Using low-spin molecular energy value, see ref 1 for discussion.

^b Estimated from $\text{p}K_a$ values in ref 26.

Conclusions

The ΔH values derived from the calculated molecular energies reproduce reasonably accurate energy requirements for metal-carbonyl, metal-hydride, and metal-metal bond dissociation and trends therein for several representative cases. Comparison of our $\text{MnX}(\text{CO})_5$ calculations with the report of Lichtenberger and Brown shows that MEHT gives results qualitatively similar to the more sophisticated nonempirical Fenske-Hall method but more accurately reproduces the relative stabilizing capabilities of various ligands.

This ability to reproduce relative effects of various substituents on a complex for a specific reaction is being further investigated for a number of systems. In addition, preliminary results suggest that comparison of calculated energies for alternate reaction pathways, substitution in complexes as but one example, may allow the prediction of the dominant pathway and suggest new chemistry to be explored.

Acknowledgment. We thank Dr. A. Anderson for providing details of the modified extended Hückel theory (MEHT) and Dr. F. Van Catledge for helpful discussions.

Registry No. $\text{MnH}(\text{CO})_5$, 16972-33-1; $\text{Mn}(\text{CO})_6^+$, 21331-06-6; $\text{Mn}(\text{GeH}_3)(\text{CO})_5$, 25069-08-3; $\text{Mn}(\text{SnH}_3)(\text{CO})_5$, 71500-59-9; $\text{Mn}(\text{PH}_3)(\text{CO})_5^+$, 71500-58-8; $\text{Mn}(\text{CH}_3)(\text{CO})_5$, 13601-24-6; $\text{MnI}(\text{CO})_5$, 14879-42-6; $\text{MnBr}(\text{CO})_5$, 14516-54-2; $\text{MnCl}(\text{CO})_5$, 14100-30-2; $\text{Mn}(\text{SH})(\text{CO})_5$, 59390-73-7; $\text{Mn}(\text{CH}_3\text{C}(\text{O}))(\text{CO})_5$, 13963-91-2; $\text{Mn}(\text{CO})_5^+$, 71563-56-9; $\text{CoH}(\text{CO})_4$, 16842-03-8; $\text{FeH}_2(\text{CO})_4$, 12002-28-7; $\text{FeH}(\text{CO})_4$, 71516-14-8; $\text{Mn}_2(\text{CO})_{10}$, 10170-69-1; $\text{Co}_2(\text{CO})_8$, 10210-68-1; $\text{Fe}_2\text{H}_2(\text{CO})_8$, 71500-60-2; $\text{Fe}_3(\text{CO})_{12}$, 17685-52-8; $\text{FeH}(\text{CO})_4^-$, 18716-80-8.

References and Notes

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Thermodynamic and Spectroscopic Properties of Mixed Complexes in Aqueous Solution. Copper(II) Complexes of 2,2'-Bipyridyl and Iminodiacetic or Pyridine-2,6-dicarboxylic Acid

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Potentiometric, calorimetric, and EPR investigations on the simple and mixed complexes of copper(II) with iminodiacetate (ida) or pyridine-2,6-dicarboxylate (dipic) anions and 2,2'-bipyridyl (bpy) were carried out. On the basis of the data obtained, the two ternary complexes $\text{Cu}(\text{bpy})(\text{dipic})$ and $\text{Cu}(\text{bpy})(\text{ida})$ turned out to have a different coordination number and stereochemistry; in particular the former appears to be octahedrally six-coordinated while the latter is five-coordinated having a square-pyramidal geometry.

Introduction

Previously,^{2,3} we reported the thermodynamic and spectroscopic properties of some ternary complexes of Cu^{II} with 2,2'-bipyridyl and some alkane or aromatic dicarboxylic acids. Considering the thermodynamic and spectroscopic (EPR and electronic) data, it was possible to observe that all the mixed complexes had the same structure because of the conformation requirements of 2,2'-bipyridyl ligand, the only exception being the complex with succinate anion, for which a square-pyramidal structure has been proposed.

In light of these results we have studied the thermodynamic and spectroscopic (EPR and electronic) parameters of mixed complexes of copper(II) with 2,2'-bipyridyl (bpy) having the same formula, $\text{Cu}(\text{bpy})(\text{L})$, as the above mentioned ones, where L is now a tridentate ligand, namely, iminodiacetate (ida) or pyridine-2,6-dicarboxylate (dipic) anion.

It was therefore possible to estimate the effects of the different denticity of the ligands (bpy as bidentate and ida or dipic as tridentate) around the copper(II) ion and of the presence of different substratum of the tridentate ligands on the thermodynamic properties associated with the formation of ternary complexes, as well as the effects on their structural parameters.

The potentiometric (pH and pCu type) and calorimetric measurements were carried out in aqueous solution at 25 °C and 0.1 mol dm^{-3} NaClO_4 . The thermodynamic and spectroscopic data were compared with those of the corresponding parent complexes measured under the same experimental conditions. We have also obtained all the thermodynamic parameters associated with the formation of the protonated and hydroxo species of the simple complexes of Cu^{II} with the tridentate dicarboxylic acids as well as the ΔH° and ΔS° values for the formation of the protonated complexes Cu -

$(\text{bpy})(\text{H})(\text{ida})$ and $\text{Cu}(\text{bpy})(\text{H})(\text{dipic})$ by using previously reported potentiometric data.⁴

Experimental Section

Chemicals. The 2,2'-bipyridyl (Erba RPE) was recrystallized from a water-ethanol mixture. The pK value found was in agreement with the value previously determined.⁵ Iminodiacetic (BDH) and pyridine-2,6-dicarboxylic (Fluka) acids were recrystallized from water. The purity of these acids was checked by titrations with standard CO_2 -free NaOH and in all cases a value higher than 99% was found. The disodium salts of these acids were prepared according to literature. The preparation of the solid simple and mixed complexes has been described elsewhere.^{6,7} All the solutions were prepared with twice-distilled water and their ionic strength was kept at 0.1 mol dm^{-3} by addition of NaClO_4 . The standardization of the solutions was carried out as previously described.²

Emf Measurements. The potentiometric measurements were carried out by means of two potentiometers (Amel 232 or Radiometer PHM 52) using a glass electrode (Ingold 201 NS) or a copper-selective electrode (Amel 201 sens-ion) and a double junction calomel electrode (Orion 90-02-200). In Table I the experimental details of potentiometric titrations are reported. Other details are as previously described.^{4,5,8,9}

Calorimetric Measurements. The calorimetric measurements were carried out at 25 ± 0.001 °C employing a LKB precision calorimeter (Model 8700) and a 100- cm^3 titration vessel (Model 8726-1). The reproducibility of the system and other details have already been reported.¹⁰ Experimental details of the calorimetric titrations are listed in Table II.

Spectroscopic Measurements. First-derivative EPR X-band spectra were recorded with a Varian E-109 instrument equipped with a standard temperature control unit. All measurements reported here were made at 133 K by using quartz sample tubes. The solutions were prepared by dissolving the solid complexes in water-methanol mixtures (1:1 ratio) and their concentrations ranged from 1 to 3 mmol dm^{-3} . Field calibration was checked by using polycrystalline di-