were 1.90 Å. In every case C_{ac}–C_{ac} was 1.38 Å, C–O = 1.16 Å, and C–H = 1.09 Å.

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Bonding and Isomerization in Fe(CO)₅

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Molecular orbital calculations in a MINDO type procedure are reported for Fe(CO)₅ in a trigonal bipyramid (TB), square pyramid (SP), and points along a Berry pseudorotation path between the two configurations. The metal d orbitals are found to contribute some to intermediate energy level molecular orbitals to shift the relative extent of axial and equatorial bonding in a way that has not been predicted from the usual symmetry orbital overlap picture. This shift is critical to obtaining axial Fe–C bond lengths in agreement with experiment, which ab initio calculations have failed to obtain. The potential energy curve between the TB and SP configurations does not contain a barrier. In the orbital energy curves between the structures, no single orbital or particularly small group of orbitals can be isolated as responsible for the greater stability of the TB over the SP geometry.

Transition-metal carbonyl chemistry is a rich and varied field.[1,2] Pentacoordinate transition-metal complexes have often been suggested as intermediates in the dissociative reactions of hexacoordinate complexes and in the associative first step in reactions of tetracoordinate compounds. The case of Fe(CO)₅ presents a stable pentacoordinate molecule with two geometries very close together in energy. NMR data indicate that the barrier to exchange of axial and equatorial ligands is no more than about 1 kcal/mol.[3] The exchange mechanism has most often been ascribed to the Berry pseudorotation mechanism,[4] with which NMR data for exchange in many pentacoordinate complexes are consistent.[5] The Berry mechanism consists of a least motion path between the trigonal-bipyramidal (TB) and square-pyramid (SP) geometries. While there have been calculations of the TB and SP structures themselves,[6–12] there have not previously been calculations of the energy along the Berry path to determine if the SP structure corresponded to a metastable reaction intermediate or to a transition state. If the latter situation prevails, then the activation energy for the axial–equatorial exchange is simply the difference in energy between the TB and SP structures. Otherwise the difference in energy between the TB and SP geometries is not simply related to the activation energy for exchange.

In previous ab initio SCF calculations that have attempted to optimize geometries there has been difficulty with the axial Fe–C bond length being considerably too long.[6,10] These works stated that they had no explanation for the long axial Fe–C bond. The calculations presented here indicate that the relative axial and equatorial bond strengths are related to the d-orbital interactions even though the total bond strengths are primarily due to iron s and p orbitals.

A variety of roles have been assigned to the d orbitals in transition-metal bonding. Adsorption on metal surfaces has been treated as if the primary bond to the surface was due to d orbitals.[13,14] In coordination chemistry symmetry orbital and orbital overlap models have been developed that assign most of the d-electron charge to nonbonding or slightly antibonding molecular orbitals that are largely d orbital in character.[7] This model has been successful in rationalizing many data. Recent semiempirical, Xα, and ab initio SCF calculations have metal s- and p-orbital interactions being primarily responsible for metal–ligand bonding.[15] In calculations for NiH₂, the d orbitals have been found to play a major role in the formation of bent metastable states that may be precursors to H₂ dissociation.[16] In this paper the nature of the d-orbital interactions that affect the bonding in Fe(CO)₅ are examined.

Calculational Procedure

The calculations were done with a semiempirical SCF method that is a modification of MINDO referred to as MINDO/SR. The details of the method as well as its ability to handle a wide variety of compounds including large metal clusters have been reported previously.[16–18] The MINDO/SR procedure explicitly includes electron–electron repulsions and is parametrized to give bond energies and lengths for selected reference compounds in agreement with experimental values.

The computer program used is based on QCPE Program 290 by Rinaldi as modified by Schmidling[19] to incorporate MINDO/3 and Vibrational calculations. The Rinaldi program has automatic geometry optimization using analytically calculated gradients. The Schmidling version was modified to incorporate transition metals, symmetry,[20] and selective molecular orbital filling.

Atomic parameters for Fe are given in Table I. These parameters are similar to the ones used previously.[17] Adjustments were made in the Fe 4p-orbital exponent, which was lowered from the Clementi and Raimondi[21] value, in the d-orbital energy, and in a Slater–Condon parameter by de Brouckere.[22] These adjustments were made to obtain

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Table I. Atomic Parameters for Iron

	orbital exponents[21]			core parameters,[22] eV		
	s	p	d	W_{ss}	W_{pp}	W_{dd}
	1.3585	1.2[a]	3.7266	−102.13	−74.57	−133.29[a]

	Slater–Condon parameters,[22] eV					
	(3d,3d)	(3d,4s)	(3d,4p)	(4s,4s)	(4s,4p)	(4p,4p)
F^0	17.727 86[a]	13.749 49	10.076 14	12.484 22	9.583 63	8.280 28
F^2	8.414 23		0.676 93		2.452 89	
F^4	5.106 33					
G^1			0.250 98		2.201 64	
G^2		1.384 66				
G^3			0.165 81			

[a] Value different from reference value.

Table II. Bond Parameters

	Fe–C		Fe–O	
	set 1	set 2	set 1	set 2
β	0.553	0.570	1.417	1.096
α	0.976	1.030	2.297	1.674

better correlation between properties for diatomic molecules and clusters containing 12 iron atoms.

The bond parameters are given in Table II. In these calculations the β parameters for s, p, and d orbitals are the same. The variation of the p-orbital exponent has the effect of taking care of differences in bonding between s and p orbitals. The Fe–O bond parameters were selected to give molecular FeO a binding energy of 90 kcal/mol and a bond length of 1.63 Å in agreement with experimental values[23] for our calculated ⁵Δ ground state. The ground state of FeO has not been definitely established and is the subject of considerable controversy.[24-27] The Fe–C bond parameters are designed to give Fe(CO)₅ with an average Fe–C bond dissociation energy into Fe + 5 CO of 28 kcal/mol and an equatorial Fe–C bond length of 1.83 Å, in agreement with experimental values.[28,29]

Results and Discussion

Molecular properties for Fe(CO)₅ in TB symmetry calculated by using set 1 and set 2 parameters and in SP symmetry calculated by using set 1 parameters are given in Table III. The orbital energies for the valence-shell orbitals are given in Table IV.

As noted in the introduction a variety of roles have been ascribed to the d orbitals in the bonding of carbonyls. For this calculation listed in Table III the Fe–C bond is largely due to the s and p orbitals on the Fe atom since the d-orbital contribution to the total Mulliken bond order is only about 5%. Another way of assessing the d-orbital contribution to the bonding is to make the bonding parameter β for the d orbitals in the Fe–C bond equal to 0.01 so that the d orbitals, while present, cannot contribute to the bonding. The result of this is to reduce the energy of atomization of Fe(CO)₅ by 50 kcal/mol if the geometry is unchanged and by 30 kcal/mol if the geometry is allowed to relax to new equilibrium positions for all atoms. In the comparison of these energy reductions to an energy obtained from the 5% d bond order, the problem of what energy to reduce by 5% arises. The calculations produce total energies of atomization and the bond energy for CO is certainly different in Fe(CO)₅ from that in a gas-phase CO molecule. To arrive at a CO bond energy in Fe(CO)₅, a bond energy–bond order correlation given in Table V, where all numbers are from MINDO calculation, may be used. These numbers produce an average Fe–C bond energy of 47 kcal/mol (as opposed to the 28 kcal/mol for the process Fe(CO)₅ → Fe + 5CO), which, when multiplied

by 5% for the d-orbital contribution in Fe(CO)₅, gives 12 kcal/mol for the total bond energy reduction of the five Fe–C bonds. The considerable difference between 12 and 30–50 kcal/mol suggests that the d orbitals have a role in the bonding that is in addition to a simple additive contribution to the bond order. In the calculation where the d-orbital bonding is eliminated, the top e′ and e″ orbitals each contain 4 electrons and are essentially pure d orbitals with the d_{z^2} orbital being empty. This closely matches the symmetry and overlap model presented by Rossi and Hoffmann.[7] In our normal calculation there are significant deviations from this picture although it remains a good first approximation. This is in keeping with the cautionary note by Rossi and Hoffmann that more detailed calculations could shift the bonding picture; in our case the more detailed calculations primarily involve explicitly including electron–electron repulsion terms.

The subtle role that d orbitals can play in bonding is most readily seen by comparing the results for parameter sets 1 and 2. The difference between these parameter sets is in the valence-state ionization potential (VSIP) for the d orbitals on the Fe atom with the consequent β and α differences. Set 2 has a literature value[22] for the d-orbital VSIP and an axial Fe–C bond length much too long as found in ab initio SCF[6] and semiempirical[10] calculations. The authors of these other calculations stated that they had no explanation for the long axial bond. In parameter set 1 the VSIP for the d orbital is changed slightly to make the d orbitals more stable. The net result is to shorten the axial Fe–C bond to bring its length into agreement with experiment. Comparing lines 1 and 2 of Table III shows that a small increase in the stability of the atomic d orbitals results in (1) a total gain of 0.36 d electron on Fe, (2) a gain of 0.14 electron in the d_{z^2} orbital, and (3) a net loss 0.21 electron in the iron sp orbitals with most of the loss occurring in the equatorial iron p_x and p_y orbitals. This shifting charge results in a decrease in the equatorial Fe–C bond orders and an increase in the axial bond orders. The bond order changes are mostly in the sp orbitals but some are in the d orbitals. Thus the main result of a small change in the d-orbital stability is a change in the relative bond strengths of the axial and equatorial Fe–C bonds of the sp orbitals.

The effect of increasing the d-orbital stability is not so much to increase the d-orbital occupancy in the top-lying nonbonding and antibonding d orbitals but is rather the more subtle effect of increasing the extent of d-orbital hybridization in middle-level orbitals, which affect the sp-orbital bonding to the axial and equatorial ligands. Using set 1 parameters rather than set 2 results in increased mixing of d orbitals into the 5e′, next to the top e′, molecular orbital and a corresponding decrease in the iron p_x and p_y contribution. This brings about the lowered iron p_x and p_y occupancy with attendant decreased bonding to the equatorial carbonyl ligands noted in the previous paragraph. In the symmetry overlap picture of Rossi and Hoffmann[7] the top e′ orbital (6e′ here) is primarily d with a small antibonding admixture of ligand σ orbitals. If set 2 parameters are used, the carbon σ orbitals in 6e′ are essentially empty so the results are essentially like the symmetry overlap picture. However, if set 1 parameters are used, the $d_{x^2-y^2}$ and d_{xy} orbitals are about equally represented in 5e′ and 6e′ and in 6e′ the coefficient for the carbon p_x (Fe–C bonding)

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Table III. Calculated Properties of $Fe(CO)_5$

molecule	parameter set	geometry	binding energy, kcal/mol	equil bond length, Å			
				Fe–C(eq)	Fe–C(ax)	C–O(eq)	C–O(ax)
I	1	TB	1357.9	1.83	1.82	1.16	1.16
II	2	TB	1356.6	1.81	1.97	1.16	1.15
III	1	SP	1355.8	1.84	1.78	1.16	1.16
IV	$\beta_d = 0.01$	TB	1315.0	1.83	1.82	1.16	1.16

molecule	atomic population					bond order			
						Fe–C(eq)		Fe–C(ax)	
	Fe	C(eq)	C(ax)	O(eq)	O(ax)	sp	d	sp	d
I	9.80	3.13	3.14	6.51	6.51	1.09	0.03	1.04	0.05
II	9.63	3.13	3.27	6.51	6.45	1.19	0.05	0.94	0.02
III	9.79	3.15	3.07	6.50	6.53	1.04	0.04	1.18	0.04
IV	9.71	3.14	3.18	6.50	6.51	1.09	0.00	1.04	0.00

molecule	Fe Mulliken population									
	s	p_x	p_z	p_y	d_{z^2}	d_{xz}	d_{yz}	$d_{x^2-y^2}$	d_{xy}	d(total)
I	0.43	0.42	0.42	0.44	0.17	1.99	1.99	1.97	1.97	8.09
II	0.48	0.50	0.50	0.44	0.03	1.98	1.98	1.86	1.86	7.73
III	0.43	0.43	0.43	0.42	1.96	1.98	1.98	0.16	1.99	8.07
IV	0.44	0.41	0.41	0.45	0.00	2.00	2.00	2.00	2.00	8.00

Table IV. Orbital Energies, au (eV), and Symmetries for $Fe(CO)_5$

Trigonal Bipyramid

a_1'	a_2'	a_2''	e'	e''
–1.273 (34.64)	–0.523 (14.23)	–1.259 (34.26)	–1.231 (33.50)	–0.540 (14.69)
–1.161 (31.59)		–0.763 (20.76)	–0.744 (20.24)	–0.517 (14.07)
–0.865 (23.54)		–0.537 (14.61)	–0.544 (14.80)	–0.466 (12.68)
–0.660 (17.96)		–0.421 (11.46)	–0.524 (14.26)	
–0.486 (13.22)			–0.442 (12.03)	
–0.345 (9.39)			–0.381 (10.37)	

Square Pyramid

a_1	b_1	b_2	e
–1.275 (34.69)	–1.161 (31.59)	–0.546 (14.86)	–1.250 (34.01)
–1.224 (33.31)	–0.659 (17.93)	–0.514 (13.99)	–0.759 (20.65)
–0.867 (23.59)	–0.522 (14.20)	–0.487 (13.25)	–0.539 (14.67)
–0.736 (20.03)	–0.344 (9.36)		–0.531 (14.45)
–0.547 (14.88)			–0.521 (14.18)
–0.488 (13.28)			–0.445 (12.11)
–0.448 (12.19)			–0.408 (11.10)
–0.371 (10.09)			

Table V. Bond Energy–Bond Order Correlation for CO

	bond energy, kcal/mol	bond order	R(C–O), Å
molecular CO	244	1.99	1.133
CO in $Fe(CO)_5$	225[a]	1.84	1.161

[a] Calculated as 244 × 1.84/1.99.

Figure 1. Potential energy along the Berry pseudorotation path from TB to SP structure.

is similar to that for the carbon s (Fe–C antibonding) so the result is a nonbonding contribution from 6e′ to the Fe–C bond. The suggestion that iron p- and d-orbital hybridization could be important has been made previously,[7] but it was considered primarily for π bonding, which does not make much contribution here.

The d_{z^2} orbital in the symmetry overlap picture contributes only to an empty a_1' molecular orbital, which is axial antibonding. Calculations with set 2 parameters reproduce this condition. On the basis of set 1 parameters, the d_{z^2} orbital contributes to the highest filled a_1' molecular orbital and is bonding for the Fe–C bond while the other components of that a_1' orbital are nonbonding contributions to the C–O bond. This increased axial Fe–C bonding is reflected in the increased d bond order based on set 1 parameters.

These considerations of the role of d orbitals illustrates one useful aspect of semiempirical calculations that when calculated properties deviate from experimental ones, changes can be made in parametrization to see what factors most strongly affect particualr properties. In the ab initio calculations the reason for the unexpected calculation of a too long axial bond was not apparent.
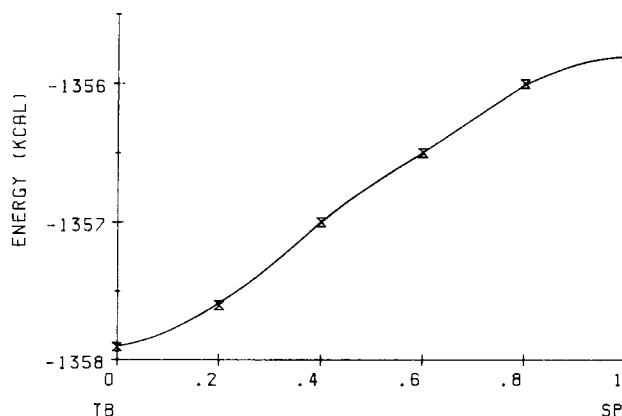
In the ab initio calculation the d levels are affected by the basis set choice. The orbital exponents, which are most often chosen from an energy minimization for an atom and not for a molecule, affect nuclear attraction and electron–electron repulsion integrals, which determine orbital energy levels. In molecules the attraction of ligand nuclei will expand d orbitals and lower orbital energy levels. Rather than changing basis sets in a single determinant wave function, a configuration interaction (CI) calculation often is performed wherein this problem is corrected because of the
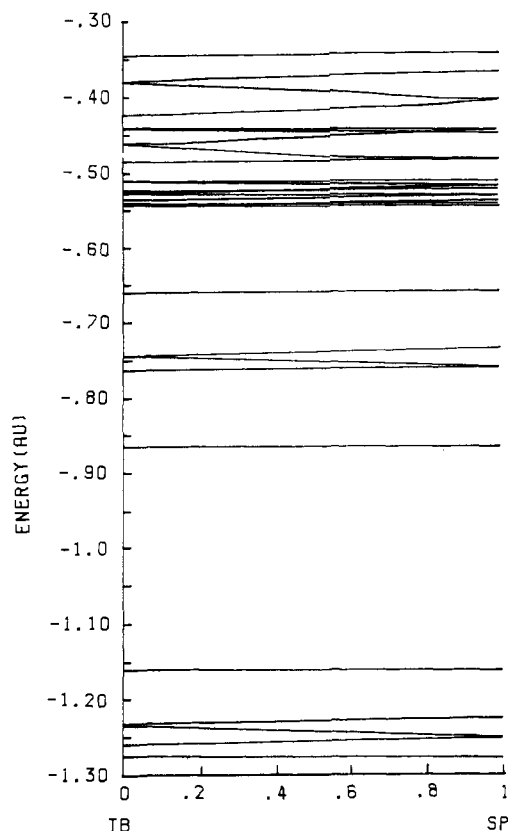
Figure 2. Orbital energies along the Berry pseudorotation path from TB to SP structure.

additional components to the wave function in the expanded calculation.

The question has been raised[6] as to whether the square-pyramid (SP) geometry represents a metastable state at the bottom of a potential well or is a transition state at a saddle point on the potential energy surface. The potential curve in Figure 1 for the energy along a Berry pseudorotation path from TB to SP shows the SP geometry at the maximum. Along the reaction path all Fe–C–O groups stay linear and from one point to the next in Figure 1 the C–Fe–C bond angles change by only 3°. At each point the angles are fixed while the energy is minimized with respect to the bond lengths. Thus, as has been previously sug-

gested[6] but left unsupported by calculation, the activation energy for ligand interchange between equatorial and axial positions is just the energy difference between the TB and SP geometries for the Berry pseudorotation mechanism. The calculated difference between the two geometries is 2.0 kcal/mol, which is in agreement with the estimate of 1 kcal/mol from NMR data.

The orbital level changes for the geometry change from TB to SP along the Berry path are shown in Figure 2. This figure does not readily lend itself to any simple interpretation of why the TB structure is more stable than the SP structure. No orbital changes much in energy, and several orbitals increase while others decrease in energy. Thus, no particular orbital energy change can be singled out as primarily responsible for the overall energy difference.

Conclusions

Although the symmetry orbital overlap picture of the metal d orbitals making their main contribution to the highest occupied e′ and e″ molecular orbitals is a good first approximation, the d orbitals influence the nature of the bonding by also contributing to the lower lying orbitals in $Fe(CO)_5$. That the d orbitals will mix with the lower lying bonding orbitals is well known and in this paper the precise consequences of that mixing are delineated. In the symmetry orbital overlap picture this hybridization is discussed in terms of stabilizing these orbitals but not changing the bonding produced by them. In $Fe(CO)_5$ the calculations here show that the addition of d character to the 5e′ orbital reduces the iron p-orbital participation and thereby changes the relative axial to equatorial bonding of Fe–C bonds. While the direct d-orbital contribution to bonding is small, it is not insignificant as in the d_{z^2} contribution to the highest filled a_1' orbital. Nonetheless, the most important effect of the d-orbital mixing is not as a direct contribution to bonding but rather in affecting the relative axial vs. equatorial bonding.

The potential energy curve between the TB and SP structures along a Berry pseudorotation path does not have a barrier so the activation energy for ligand exchange between axial and equatorial positions is just the difference in energy between the TP and SP geometries. In the orbital energy curves between the structures, no single orbital or small group of orbitals can be isolated as responsible for the greater stability of the TB over the SP geometry.