M-O distances, with the rest of the molecule rigid". Goddard has developed a modified GVB (M-GVB) program which uses empirical corrections for certain two-electron integrals, and by using this program he has calculated a short bond for Cr_2.[44] These systems are very difficult to describe theoretically, and experience has shown that an isolated calculation can get the "right" answer for the wrong reason. It would be useful to know how well these methods handle the well-studied trends, rather than isolated controversial cases.

Conclusion

GVB calculations do not provide correct absolute values for Cr-Cr bond length, but they do provide wave functions with the correct physical properties, which we may use to accurately predict trends. Therefore, we cannot predict a priori Cr-Cr bond lengths, but we can indicate responses of Cr-Cr bond lengths to changes in bridging ligation and relative responses to axial ligation. Our calculations indicate that the Cr-Cr bond length in anhydrous dichromium tetraacetate should be longer than either the amidato or amidinato complexes. Our calculations of the response of Cr-Cr bond length both to changes in the bridging ligands and relative changes in Cr-Cr bond length upon axial ligation are consistent with a Cr-Cr bond length of 2.05-2.10 Å for dichromium tetraacetate. We also conclude that the bridging and axial ligands do not effect the Cr-Cr bond length independently but cooperatively. Bridging ligands with lower electronegativity result in shorter Cr-Cr bonds, but they also make the change in bond length upon axial ligation greater.

Acknowledgment. We than the National Science Foundation (Grant No. CHE 86-19420) and the Robert A. Welch Foundation (Grant No. A-648) for support of this work. This research was conducted in part with use of the Cornell National Supercomputer Facility, a resource for the Center for Theory and Simulation in Science and Engineering at Cornell University, which is funded in part by the National Science Foundation, New York State, and the IBM corporation. We also gratefully acknowledge Cray Research, Mendota Heights, MN for a generous grant of computer time.

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Noncatalyzed, Homogeneously Catalyzed, and Heterogeneously Catalyzed Formyl Formation

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Abstract: Potential energy surfaces have been calculated for H migration onto a carbonyl to give a formyl structure for a noncatalyzed, a homogeneously catalyzed, and a heterogeneously catalyzed reaction using a semiempirical MINDO procedure. For the $H_2 + CO$ reaction to give formaldehyde, the high activation energy is due to the fact that, in the limited orbital space available, the H-H bond must be almost entirely eliminated before the two H atoms are far enough apart to both form strong bonds with the carbon atom. For the homogeneous reaction $(CO)_4FeH^- \rightarrow (CO)_3FeCHO^-$ the activation energy is reduced to 44 kcal/mol because the H maintains bonding with the Fe while the C-H bond is forming, but the activation energy is still high because the highest occupied molecular orbital of the formyl product is an energetically unsuitable place to put electrons. In the heterogeneous process $HFe_{12}CO \rightarrow Fe_{12}CHO$, the activation energy is reduced to 5 kcal/mol because the H and C interaction with the large number of orbitals in the Fe sp band accommodates the changing H and C geometry and bonding with relatively little energy change. The consequences of this explicit comparison of homogeneous and heterogeneous catalysis are discussed.

The nature of the catalytic process has been a concern of chemists since chemistry became an experimental science. In 1836 Berzelius[1] brought together the known observations on enhanced chemcial activity, and to focus attention on the phenomena, he gave it a name, catalysis. For convenience he designated a causitive agent as the catalytic force but clearly indicated that the phenomena were rooted in the standard electrochemical affinities of matter. Current reaction rate theory (activated complexes on a potential energy surface) in conjunction with thermodynamics (the catalyst does not formally appear as a reactant or product and so cannot affect initial and final states, i.e. equilibrium) designates the role of the catalysts in enhancing a reaction rate as providing an alternative reaction path that has a lower activation energy.[2,3]

At the heart of catalysis, then, is the determination of potential energy surfaces (PES) for reactions and definition of those factors that cause different reaction channels to have different barrier heights. Ultimately, reactivity must be treated as a dynamic process, but it has been noted that the major limitation to the accuracy of all the classical, quantum, and statistical dynamics methods comes from the quality of the potential energy surface used. In this paper the fundamental nature of the catalytic process is probed by determining the PES for one reaction (the addition of hydrogen to the carbon atom of a carbonyl group) in two metal-catalyzed processes and in a noncatalyzed reaction.

Because catalysis is such a widely used and economically important industrial process, there is a great deal of practical empirical knowledge about catalytic reactions but relatively much less understanding of the mechanistic details of these catalytic reactions. As a starting point to a molecular understanding of metal-catalyzed reactions, an analogy between homogeneous and heterogeneous reactions often has been proposed.[4] The molecular orbital model for chemisorbed CO,[5,6] which has been highly

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successful in treating many aspects of CO adsorption on metals, was implicitly based on molecular orbital models of coordination complexes. In this paper the homogeneous–heterogeneous connection is directly probed by determining the PES for the addition of hydrogen to a carbonyl group both in a mononuclear coordination complex and on the surface of a metal cluster. The PES for each of the following three reactions has been determined.

$$H_2 + CO \rightarrow H_2CO \qquad (1)$$

$$(CO)_4FeH^- \rightarrow (CO)_3FeCHO^- \qquad (2)$$

$$HFe_{12}CO \rightarrow Fe_{12}CHO \qquad (3)$$

There exists a substantial body of organometallic literature dealing with alkyl migration reactions to form acyls.[7] The smallest unit that might be considered to migrate is a hydrogen atom. Athough many transition-metal alkyls readily migrate to an adjacent carbonyl to form an acyl, the rearrangement of a transition-metal hydride to a formyl has not been observed.[8-10] The formyl complex $[(CO)_4FeCHO]^-$ was first synthesized from $Na_2Fe(CO)_4$ in 1973.[11] Subsequently, many transition-metal formyls have been reported, but most have a half-life near room temperature in the range from seconds to a few days.[8,12] In spite of the reluctance of transition-metal hydrides to shift the hydrogen atom to a CO to give a metal formyl, formyl complexes have been suggested as intermediates in the catalytic reduction of CO with hydrogen.[13-15]

A PES has been calculated for the hydrogen transfer in a coordination complex per reaction 2 using semiempirical calculations referred to as MINDO/SR.[16] While the energy for individual structures of a mononuclear transition-metal complex can certainly be calculated by ab initio quantum mechanics, the use of a semiempirical method is the most efficient way to obtain many points along a reaction path on a PES. Because of the great difficulty in theoretically handling a localized adsorption interaction on an extended metal surface at a sophisticated enough level to get accurate electronic properties, the use of clusters of 1–50 metal atoms to represent the metal surface has developed into a widely used procedure.[17-19] In previous work the interactions of a hydrogen atom[20,21] and CO[21] with a 12-atom iron cluster representing the (100) face of Fe by the semiempirical MINDO/SR procedure have been calculated and found to be in good agreement with experimental observations. Through an examination of the diatomic energy terms, the coadsorption of CO and H in proximity to each other was found to affect the energetics of their interaction with the surface. In this paper calculations are presented for the next step, which is the determination of a PES for adsorbed H migration onto adsorbed CO to form an adsorbed formyl as in reaction 3.

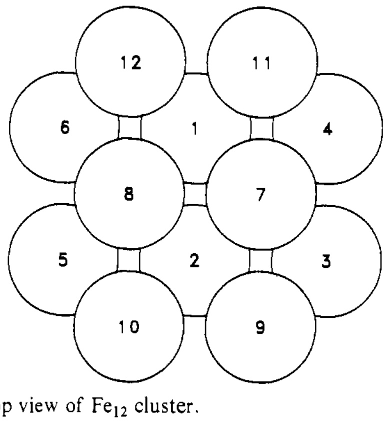

Figure 1. Top view of Fe_{12} cluster.

Table I. Parameters for Iron

(a) Orbital Exponents[28]

	ζ_1	C_1	ζ_2	C_2
4s	1.1[a]	1.0		
4p	1.1[a]	1.0		
3d	6.06828	0.40379	2.61836	0.71984

(b) Core Parameters,[29] eV

W_{ss}	W_{pp}	W_{dd}
−102.13	−74.57	−129.29[a]

(c) Slater–Condon Parameters,[29] eV

	(3d,3d)	(3d,4s)	(3d,4p)	(4s,4s)	(4s,4p)	(4p,4p)
F^0	17.727 86[a]	13.205 28[a]	10.076 14	13.028 42[a]	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 56				
G^3			0.165 81			

(d) Bond Parameters

	Fe–Fe	Fe–C	Fe–O	Fe–H
β	0.273	0.729	1.710	0.418
α	0.382	1.571	3.515	1.517

[a] Value different from reference value.

In order to establish a perspective for the two metal-catalyzed processes, calculations using the MINDO/SR program are presented of a PES for the noncatalyzed addition of hydrogen to CO as in reaction 1. In this paper we are not concerned with overall processes of molecular H_2 adding to carbon monoxide but rather are concerned only with the single mechanistic step of a hydrogen atom migrating from an initial partner onto a CO moiety and which process is expected to be the rate-determining step in overall processes. In reactions 2 and 3 the migrating H atom starts out attached to a metal atom. In reaction 1 the migrating H atom starts out attached to another H atom and then proceeds to migrate onto the carbonyl group to give a formyl group, which is part of a formaldehyde molecule. The combination of these results produces a direct comparison of the potential energy surfaces for the same process in a noncatalyzed, homogeneously catalyzed, and heterogeneously catalyzed mechanism.

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.[20-24] 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 decomposition of the total energy into monoatomic and diatomic energy terms puts the effect of one adsorbate on another on a firm quantitative basis. Specific expressions for this partitioning have been given.[25]

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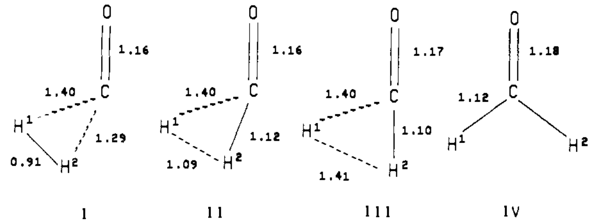

Figure 2. MINDO/3 calculated structures: I, preactivated complex; II, activated complex; III, postactivated complex; IV, formaldehyde.

The computer program used is based on QCPE Program 290 by Rinaldi as modified by Schmidling[26] to incorporate MINDO/3. The Rinaldi program has automatic geometry optimization using analytically calculated grdients. The Schmidling version was further modified to incorporate transition metals, symmetry,[27] and selective molecular orbital filling.

Atomic and bond parameters for Fe are given in Table I. These parameters were selected to give reasonable properties to FeH, FeO, $Fe(CO)_5$, $HFe(CO)_4^-$, $(CO)_3FeCHO^-$, $CH_3Fe(CO)_4^-$, $(CO)_3FeC(O)CH_3^-$, HFe_{12}, $COFe_{12}$ and OFe_{12}. The double-ζ basis for the Fe 3d orbitals is from Clementi and Roetti[28] and the d orbital energy and Slater–Condon parameters are from de Brouckere.[29] Spectroscopic terms for the F^0 ($k = 0$) Slater–Condon parameters, which contribute most significantly to the final result, are used so these are independent of the orbital exponents used. Some adjustments in these parameters were made to obtain better correlation between calculated and experimental properties for the reference compounds above. The β parameters for s, p, and d orbitals are the same.

A 12-atom cluster was chosen as being large enough to represent several types of binding sites on a Fe(100) plane and small enough that calculations could be done in a reasonable length of time. The geometric arrangement of the atoms is shown in Figure 1. Calculations were done with the Fe cluster atom positions fixed as in the bulk[30] with a nearest-neighbor distance of 2.48 Å and a next nearest distance of 2.86 Å. The atoms on the top layer are next nearest neighbors to each other and nearest neighbors to bottom layer atoms. A state with multiplicity 39 was found to give the lowest energy. The multiplicity 39 corresponds to a d^7 configuration with three unpaired electrons per atom. No magnetic data for small iron clusters are available. In view of the atomic magnetic moment of bulk Fe being 2.22 μ_B,[31] a state of high multiplicity is expected.

An on-top site is defined as an atom or molecule adsorbed directly over atom 7. In the case of CO the Fe(7)–C–O group is linear with the axis perpendicular to the plane of the top layer of atoms unless otherwise stated. A 4-fold site is defined as being directly over atom 1 with the C–O axis perpendicular to the top layer unless otherwise stated.

Symmetry and the selective filling of symmetry orbitals was not used in these calculations other than for formaldehyde and $HFe(CO)_4^-$ because, as reaction occurs, the symmetry is only C_s, which does not lead to a significant enough reduction in calculation time to be worth using. In the early phases of the calculations for transition metals, a large damping factor is required in the iterative determination of MO coefficients from the secular equation because pathologic charge oscillations occur if a damping factor is not used. These charge oscillations indicate that a variety of different MO occupations are sampled before the calculations settle down for the transition-metal calculations. For the H_2 + CO reaction complex there is only one a″ orbital (antisymmetric with respect to the molecular plane) occupied. This orbital is a π-bonding orbital for the C–O bond. The next lowest a″ orbital is a π-antibonding C–O orbital, which is high enough in energy to remain unoccupied. The energy minimization procedure occupies the lowest a′ orbitals at each geometry.

Results and Discussion

Noncatalyzed CO Hydrogenation. The main interest in the calculations in this paper is the comparison of the PES's for the three reactions. Therefore, for reaction 1, the reaction of H_2 with CO, attention is focused on determining those factors that lead to a high activation energy. To reach the structure of the activated complex, structure II of Figure 2, H^1 of the H_2 molecule approaches the CO molecule from a direction that permits it to bond strongly with the C p_x orbital as it does in the final state of formaldehyde, structure IV. As H^1 approaches the CO in structure I, the H^2 atom initially stays close to H^1 to maintain a strong H–H bond. When the H^1 atom reaches its position in the activated complex, the H^2 atom's angular displacement from H^1 is increased to separate the H atoms and the C–H^2 distance is optimized to minimize the energy along the path separating the H atoms.

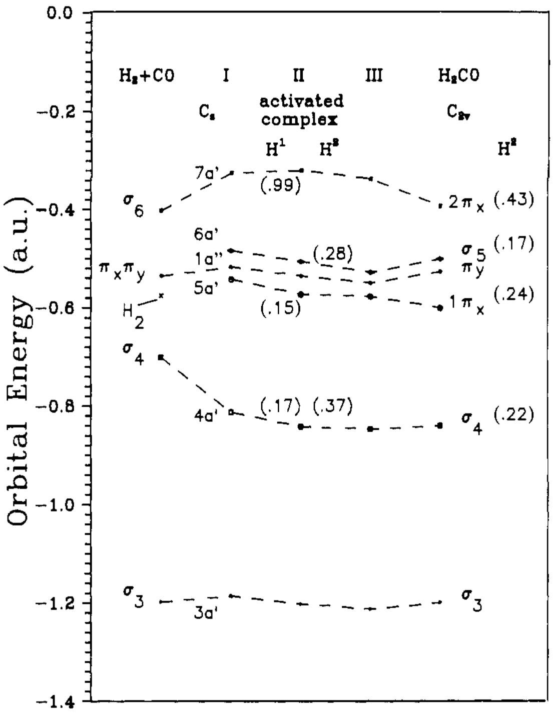

Figure 3. Orbital energies for structures in Figure 2.

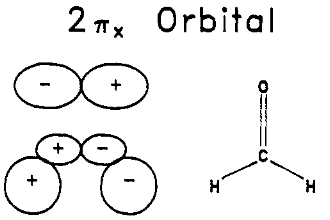

Figure 4. Diagram of $2\pi_x$ orbital of formaldehyde.

The progression from preactivated complex to activated complex to postactivated complex is shown as structures I–III, respectively, in Figure 2. The activated complex is 64 kcal/mol less stable than formaldehyde in these calculations where all parameters are standard for MINDO/3.[32] Structure II for the activated complex is very similar to that predicted by ab initio calculations utilizing CI and a large basis set,[33,34] as can be seen from the bond lengths from ref 34 given in parentheses in Table II. The ab initio calculations give an activation barrier of 87 kcal/mol. The O–C–H^1 angle in the activated complex is calculated to be 108° by MINDO/3 and 110.8° in ref 34. Thus, the geometric shape of the activated complex predicted by MINDO/3 is quite close to that of the SCF-CI calculations. The C–O and C–H^2 bond lengths are quite close for the two calculations. The difference of 0.17 Å for the C–H^1 length between the calculations is of little consequence since the distance is long enough that this interaction makes only a small contribution to the total energy. The main

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Table II. Calculated Properties for H_2 + CO, Activated Complex, and H_2CO

Monoatomic Properties

	H_2 + CO		activated complex		H_2CO	
	Q, e	*E*, au	*Q*, e	*E*, au	*Q*, e	*E*, au
C	+0.29	-4.0187	+0.42	-3.7729	+0.64	-3.5869
O	-0.29	-10.8949	-0.31	-10.9315	-0.42	-10.9672
H^1	0	-0.3415	-0.36	-0.4070	-0.11	-0.3645
H_2	0	-0.3415	+0.25	-0.2776	-0.11	-0.3645

Diatomic Properties

	H_2 + CO			activated complex			H_2CO		
	R, Å	BO[a]	*E*, au	*R*, Å[b]	BO	*E*, au	*R*, Å	BO	*E*, au
C-O	1.13	1.99	-1.1507	1.17 (1.179)	1.82	-1.0746	1.18	1.76	-1.0861
H-H	0.75	1.26	-0.4019	1.09 (1.213)	0.35	-0.1157	1.80	-0.07	+0.0156
C-H^1		0	0	1.40 (1.572)	0.41	-0.1896	1.12	1.18	-0.4388
C-H^2		0	0	1.12 (1.096)	1.04	-0.3196	1.12	1.18	-0.4388

[a] BO ≡ bond order. [b] Numbers in parentheses are from the ab initio calculation in ref 34.

contribution to the MINDO/3 activation energy being 26% less than the SCF-CI energy comes from the H-H bond being a little shorter and stronger in MINDO/3. Overall, the MINDO/3 calculation is surprisingly good in view of it being parametrized for stable molecular bond lengths and energies, with no prior consideration having been given to the longer distances found in activated complexes.

The orbital energy changes in the progression from separated H_2 + CO to structures I-III about the activated complex to the stable product H_2CO are shown in Figure 3. The molecular orbital designations for structures I-III, which have C_s symmetry, are given under the column labeled C_s. The orbital designations for H_2CO are given under the column labeled C_{2v} for its symmetry. In H_2CO the electron populations on H^2 are given as the numbers in parentheses for each orbital in the column headed by H^2. From these numbers the largest contribution to the C-H bond in H_2CO is seen to be in the $2\pi_x$ orbital, which is shown diagrammatically in Figure 4. It may be noted that the two H orbital contributions have opposite signs, so they may be considered to originate from the H_2 antibonding molecular orbital.

For the activated complex in Figure 3 the electron population of each H atom is given as the number in parentheses in the columns under H^1 and H^2. The nature of the molecular orbitals 4a′, 5a′, 6a′, and 7a′ for the activated complex is shown diagrammatically in Figure 5. The strongest bonding of H^1 occurs in the 7a′ orbital via the C p_x orbital. In all of these orbitals the signs of both H atomic orbitals are the same in all the molecular orbitals so as to maintain as strong a H-H bond as possible. This occurs in structures I-III so that the H_2 antibonding molecular orbital is not occupied at all in these structures. In the activated complex the bond between H_2 and CO is essentially a 3-center bond between the doubly occupied H_2 σ orbital and a partially filled sp hybrid orbital of the CO. The limited orbital space available places too high a charge density in a limited space to give stable bonding so the activated complex has a high energy. As can be seen in Table II, the stretched H-H bond diatomic energy is low and the two new C-H bonds are weak. In order to achieve a more stable structure, H^2 must migrate to the other side of the C atom where its orbital can change sign to bond with the other lobe of the C p_x orbital as in Figure 4, and the H-H distance is large enough that the fact that the H_2 antibonding orbital combination is occupied no longer matters. In the limited orbital space available, the H-H bond must be almost totally eliminated before the two H atoms are far enough apart to both form strong bonds with the carbon atom.

H Migration in $[HFe(CO)_4]^-$. Our MINDO/SR calculations of the energy along the reaction coordinate for the H migration in $[HFe(CO)_4]^-$ to form $[(CO)_3FeCHO]^-$ have already been published.[16] Therefore, only those results pertinent to a comparison to the noncatalyzed and the surface processes will be discussed. In the approximation of maintaining the C-Fe-C bond angles constant, the H atom migration produces a formyl that is 44 kcal/mol less stable than the metal hydride. The energy along the reaction path monatonically increases. Allowing the bond angles to relax lowers the energy of the formyl, but it is still 24 kcal/mol less stable than the hydride. Adding a CO ligand in a concerted process with the H atom migration produces a metastable formyl by a path with about a 30 kcal/mol barrier.

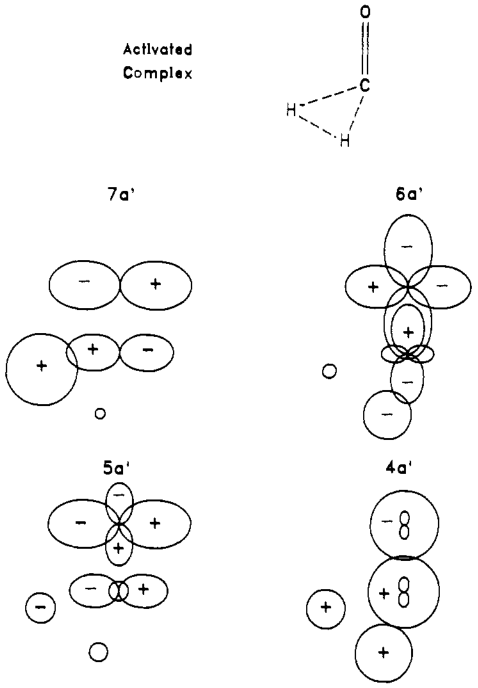

Figure 5. Diagram of orbitals for activated complex.

Thus, the addition of a H atom to CO in this case where the H atom starts out bound to an Fe atom has an activation energy about half of that for the H atom starting out bound to another H atom. The barrier for the Fe complex is mainly due to the lack of stability of the formyl complex. This is a result of the highest occupied molecular orbital of the formyl complex being high in energy, putting a large negative charge, -0.45e, on the formyl H atom, and being antibonding for the C-H bond. The basic cause of a high-energy process is the lack of a suitable orbital in which to place excess charge. As the H atom migrates it maintains a bonding relationship with the Fe atom that decreases with increasing distance and is replaced by C-H bonding, which, because of the nature of the highest occupied molecular orbital, is a weak bond. Further calculations have shown that the well-known promoting effect by alkali ions for metal to carbonyl migration[35] is due to the positive alkali ions removing charge from this high-energy orbital.[36]

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Table III. Calculated Properties for $HFe_{12}CO$, the Activated Complex, and $Fe_{12}CHO$

Monoatomic Properties

	$HFe_{12}CO^a$		activated complex^a		$Fe_{12}CHO^a$	
	Q, e	E, au	Q, e	E, au	Q, e	E, au
O	-0.45	-10.9548	-0.62	-10.9949	-0.65	-11.0080
C	+0.77	-3.7187	+0.69	-3.6860	+0.63	-3.6713
H	-0.37	-0.4080	-0.34	-0.4044	-0.39	-0.4109
Fe(7)	+0.04	-20.1420	+0.24	-20.1414	+0.28	-20.1463
Fe(8)	+0.01	-20.1343	-0.02	-20.1157	-0.01	-20.1227
Fe_{12}	+0.06		+0.27		+0.43	

Diatomic Properties

	$HFe_{12}CO^a$			activated complex			$Fe_{12}CHO^a$		
	R, Å	BO^b	E, au	R, Å	BO	E, au	R, Å	BO	E, au
C-O	1.17	1.85	-1.1538	1.21	1.62	-1.0441	1.23	1.52	-0.9896
C-H	2.89	0	-0.0476	1.45	0.44	-0.2177	1.24	0.81	-0.3547
C-Fe(8)	2.19	0.87	-0.3676	2.08	1.03	-0.4565	2.13	1.02	-0.4532
C-Fe_{12}			-0.4228			-0.4978			-0.4877
H-Fe(7)	1.80	0.92	-0.2396	2.35	0.40	-0.0863	3.03	0.09	-0.0226
H-Fe(8)	3.38	0.04	-0.0002	2.35	0.20	-0.0109	2.78	0.02	+0.0143
H-O	3.50	0.00	+0.0245	2.23	-0.02	+0.0535	1.99	-0.03	+0.0787
O-Fe_{12}			+0.0777			+0.0760			+0.0572

[a] See Figure 7. [b] BO ≡ bond order.

H Migration onto CO on Fe_{12}. For adsorption of CO and H individually and together on adjacent sites of the (100) face of the Fe_{12} cluster, the calculational results using MINDO/SR have been published.[21] Breakdown of the adsorption energy into monoatomic and diatomic terms indicated a complex interaction in which a large Fe-C diatomic energy term of 325 kcal/mol for CO in an on-top site is needed to obtain a net adsorption energy of 23 kcal/mol because of large destabilizing monoatomic energy terms and because adsorption destabilizes the Fe_{12} cluster. The cluster d band is shifted by adsorbate-adsorbent charge transfer even though the d orbitals overlap only very weakly with the adsorbate. The complexity of the adsorption interaction is such that an approximate treatment that considered only the adsorption bond might not be expected to predict the correct relative energy of adsorbate bonding at different symmetry sites. Both H and CO adsorbed separately are electron acceptors with adsorption at a 4-fold site preferred over adsorption at an on-top site. While the interaction of CO with its nearest neighbor dominates the interaction energy, the interaction energy with the other cluster atoms is necessary for a quantitative account of adsorption and can be as large as the net adsorption energy. Coadsorption of CO and H at adjacent on-top sites results in a total adsorption energy that is 7 kcal/mol less than expected for their separate adsorption. Analysis of the diatomic energy terms shows that the H is adsorbed with the same strength as when alone but that the adsorbed CO is destabilized by the presence of the H. Coadsorption of CO and H at adjacent 4-fold sites results in a 41 kcal/mol destabilization from separate adsorption. In this case the diatomic energy terms indicate that both the H and CO adsorption strengths are decreased due to their both bonding to the same Fe atoms, which are common to the adjacent 4-fold sites.

The potential energy as H migrates from an on-top site to CO at an adjacent on-top site to form a formyl at an on-top site is given in Figure 6. This process is endothermic by about 2 kcal/mol with an activation barrier of 5 kcal/mol. For each point on the curve all C, H, and O coordinates were optimized except for the x coordinate of the H atom, which defines its movement from the Fe to the C atom. The structures for the H migration onto CO on the Fe_{12} cluster are shown in Figure 7 and the orbital energies for these structures are in Figure 8.

The energy, population, and bonding results for the formyl group at an on-top site of Fe_{12} are given in Table III. The H atom contributes a gain of 10 kcal/mol to the stability of the system upon moving from the Fe on-top bonding site to the C atom in the formyl. This gain is largely due to the gain in H atom diatomic energy on going from an Fe atom to a carbon atom. The CO unit within itself has an energy destabilization of 91 kcal/mol, due mostly to the loss in C-O diatomic energy as the H bonds to the C. This energy loss is partially offset by an increase of 41 kcal/mol in the $Fe_{12}C$ diatomic energy and a gain in $Fe_{12}O$ diatomic energy of 13 kcal/mol, so that the CO unit with its Fe interaction undergoes a net loss of only 37 kcal/mol in stabilization energy. The Fe_{12} unit is stabilized by 25 kcal/mol during the migration. This change may be rationalized by noting that previous results[21] showed that both the H and CO interactions with the cluster destabilized it, so when the migration reduces the number of adsorbate cluster interactions from 2 to 1 the cluster is stabilized. Adding the H atom 10 kcal/mol stabilization, the CO unit 37 kcal/mol destabilization, and the Fe_{12} unit 25 kcal/mol

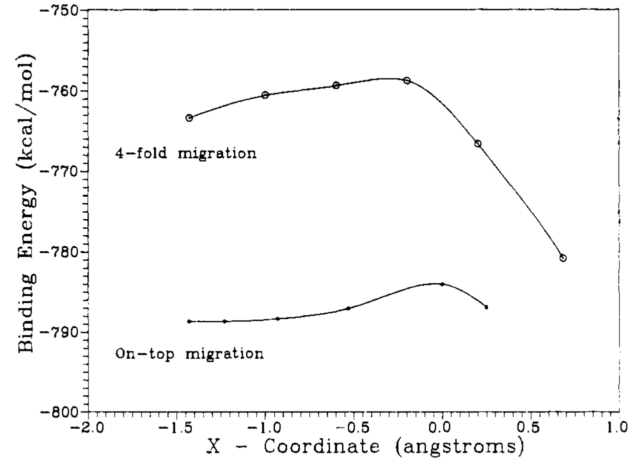

Figure 6. Binding energy for H migration from $HFe_{12}CO$ to $Fe_{12}CHO$. For the on-top migration curve the left-most point is the left structure of Figure 7; the maximum energy is for the center structure of Figure 7; the right-most point is for the right structure of Figure 7.

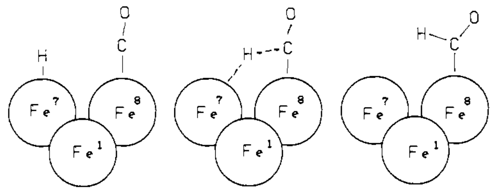

Figure 7. Key: left structure, H and CO at on-top sites of Fe_{12} with atom numbers per Figure 1; center structure, activated complex; right structure, formyl at on-top site.

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(36) Blyholder, G.; Zhao, K.-M.; Lawless, M. *Organometallics* **1985**, *4*, 2170.

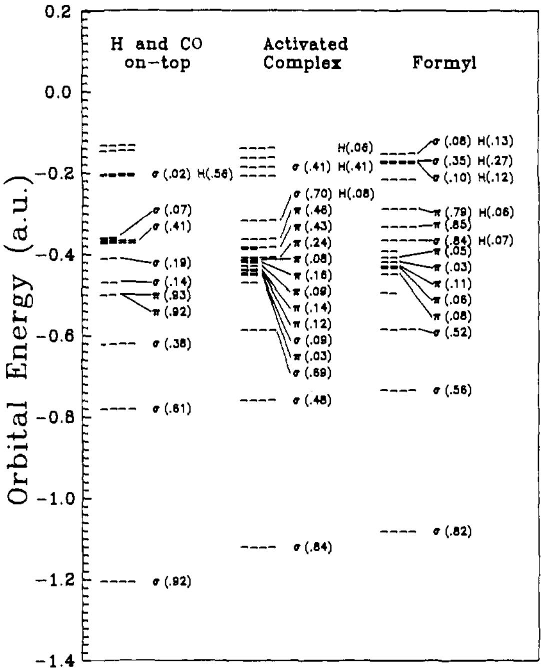

Figure 8. Molecular orbital diagram for the structures of Figure 7 on a Fe_{12} cluster. The d orbitals are indicated by short dashed lines and form a dense band between the highest and lowest d orbital (most d orbitals are not shown). The sp orbitals of Fe are indicated by longer dashed lines. The σ and π populations of CO are in parentheses. The H orbital populations are in parentheses after the symbol H. Only the majority spin set is shown.

stabilization yields a net destabilization for the H atom migration of 2 kcal/mol.

The calculational results for the activated complex at the top of the potential barrier are also given in Table III. The Fe s and p orbitals are considerably more diffuse than the C orbitals, so the energy change with distance is less for the Fe–H bond than for the C–H bond. With the H atom having moved about 80% of the way along its total motion at the activated complex, it has lost 64% of the HFe(7) diatomic energy but has gained only 55% of the HC diatomic energy in the formyl structure. This is the fundamental reason that a barrier exists between the two structures. The barrier is kept small by the H atom developing a stabilizing diatomic interaction energy with Fe(8) (to which the CO is bonded), due to the long range of the Fe–H interaction. The compensating stabilization of the Fe_{12} unit, which resulted in the formyl structure only being slightly endothermic with respect to separate adsorbed CO and H, also contributes to keeping the activated complex stable.

For the migration of the adsorbed H atom onto CO to give a formyl in a 4-fold site when both the H and CO start in adjacent 4-fold sites, the reaction path shown in Figure 6 has only a 5 kcal/mol activation energy. Even though the 4-fold adsorption sites for a single isolated adsorbate are found to be slightly more favorable than the on-top sites, the reaction using the on-top sites is much more favorable in these calculations. This is because CO and H have a considerable destabilizing influence on each other when occupying adjacent 4-fold sites. The reaction on the 4-fold site is exothermic because while the 4-fold formyl is 6 kcal/mol less stable than the on-top formyl, the 4-fold starting point is 25 kcal/mol less stable than the on-top starting point. For the CO and H on adjacent on-top sites the mutual destabilization is small. For the H migration reaction to occur most efficiently the H and CO adsorbates would migrate to adjacent on-top sites for reaction. The details of the 4-fold migration will not be discussed further since it is less favorable than the on-top migration.

Within the framework of this calculational procedure, the formation of a surface formyl from adsorbed CO and H atoms is feasible. The extent to which it actually occurs has not been established and could only be determined by examining all reaction paths available. Calculations have not yet been done for other reaction sites and other possible reactions of CO and H. Thermal desorption data do indicate that CO and H form a surface complex,[37] and these calculations indicate that formyl is a viable candidate for that complex.

Just how appropriate the calculations here with a Fe_{12} cluster are as a model for an extended metal surface is not known. There are sufficient atoms that on-top, bridging, and 4-fold sites can be distinguished. However, the surface Fe atoms that interact directly with the adsorbate do not have all of their nearest neighbors. There are edge effects in that both H and CO are more strongly bound to edge Fe atoms than to centrally located Fe atoms. Other calculations have shown variation in adsorption energy as the cluster size is varied.[38] Future calculations with larger clusters are planned. Where there is charge transfer between the adsorbate and the cluster and particularly where one adsorbate affects another, the variation in the ability of a cluster to delocalize charge with size could be important.

As a semiempirical method, MINDO calculations have given good results because of the parametrization with model compounds to reproduce binding energies and bond lengths and because electron repulsion terms are explicitly included to take charge transfer into account. Due to the complexity of transition-metal systems, while the broad aspects of these semiempirical calculations are expected to be correct, details are certainly subject to revision as more accurate calculations become available.

Comparison of Reaction Paths. For the noncatalyzed production of a formyl structure per reaction 1, the high activation energy is a result of the H–H bond having to be largely broken in the activated complex with only weak C–H bond formation. Because of the relatively compact nature of the atomic orbitals of the atoms in the first and second row of the periodic table, the movement of H^2 is only 32% of its total movement away from H^1 in the activated complex but 71% of the H^2H^1 diatomic energy has been lost and the C–H bonds have gained only 58% of their final diatomic energy. In contrast to this, on the Fe_{12} cluster the H atom has moved 80% of its total path at the activated complex, and the Fe–H bond has lost only 64% of its diatomic energy and the C–H bond has gained 55% of its diatomic energy. Further, if the interaction of the H atom with all Fe atoms in the Fe_{12} cluster is considered, the loss in HFe_{12} diatomic energy is only 41% at the activated complex. The more diffuse nature of the metal s and p orbitals and the ability of a surface ligand to have a bonding interaction with several surface metal atoms simultaneously allows the surface ligand to move parallel to the surface with relatively little expenditure of energy. The result is a much lower activation energy for the H atom migration from a Fe atom onto CO to give a surface formyl than for H atom migration from another H atom onto CO to give a formyl as part of formaldehyde.

Comparing the heterogeneous H atom migration onto a CO molecule on the surface of a Fe_{12} cluster to the same migration in $HFe(CO)_4^-$ conversion to $(CO)_3FeCHO^-$, the overall result is a much smaller activation energy for the heterogeneous process. For this particular case, a major cause of the barrier to H migration in the coordination complex is the high energy of the formyl complex. Although d orbitals and the d band of metals are frequently invoked in catalysis, the d orbitals overlap little in these calculations with the adsorbates so the Mulliken bond orders for the d orbitals are small. However, an analysis of the contribution of d orbitals to the diatomic energy terms for CO adsorbed on the Fe_{12} cluster indicates that the d orbitals are responsible for 40 to 50% of the CO adsorption energy.[39] For the Fe_{12} cluster, the d orbital populations of the Fe atoms never varied by more than a few thousandths from 7 during the adsorption and migration reaction. For the negative ion of the

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complex the Fe d population remains close to 8 during the H atom migration. However, there is some rearrangement of charge among the d orbitals of the complex during migration. The population of the d_{z^2} orbital, which is on the Fe–H axis of the hydride, increases from 0.18 in the hydride to 0.76 in the formyl. This charge comes mostly from the $d_{x^2-y^2}$ orbital. Since the d orbitals have very little overlap with the ligand orbitals, the population changes are presumed not to be due to bonding interactions lowering orbital energies but rather to repulsive interactions. In this case migration of the H atom removes the repulsive interaction of the hydride along the z axis so that after migration the d_{z^2} orbital is relatively more favored and the carbon atoms in the xy plane gain electrons to increase the repulsion in the xy plane. In the Fe_{12} cluster the various individual d orbital populations change very little during the migration. The larger ligand distances for the Fe_{12} cluster would contribute to the repulsive interactions having less effect for the cluster than for the complex.

Another important difference between the Fe_{12} cluster and the mononuclear metal complex is that the ligands interact with a band of orbitals on the cluster rather than with just a few orbitals on the complex. Orbital levels for the adsorbed CO and H and their reaction complex are given in Figure 8. In the case of the complex it was shown[36] that the migration leads to the occupation of an unfavorable high-energy orbital. Much of the H atom interaction occurred in this orbital. The d orbitals of the complex did not serve as a reservoir for charge, so that the bonding needed to be accommodated within the limited available s and p orbitals of the single Fe atom and the CO ligands. In contrast, for the cluster the CO and H interact with the broad sp band of the Fe_{12} cluster as shown in Figure 8 where the H atom contributes electron population to a number of molecular orbitals of the cluster formyl and the activated complex. Within the large number of orbitals in this band the CO and H interactions and the migration are accommodated without major orbital shifts and the migration proceeds without a large activation energy. Again, the d band of the cluster does not serve as a charge reservoir, but rather charge transfer is accomplished via the metal sp band.

Conclusions

Calculations have been carried out with a semiempirical procedure to calculate PES's for H migration onto a carbonyl to give a formyl structure for a noncatalyzed, a homogeneously catalyzed, and a heterogeneously catalyzed reaction. These calculations are consistent with the classical statement that a catalyst operates by providing a path with a reduced activation energy. The often-suggested analogy between heterogeneous and homogeneous is supported within the framework of these calculations by similarities in the H migration for the model homogeneous and heterogeneous catalytic processes, but distinct differences are also found. An important difference between the heterogeneous and homogeneous process is that the large number of orbitals in the metal valence band permits many different bonding structures with similar energies whereas the mononuclear homogeneous complex has only a few orbitals, which limits it to only a few stable structures. While this permits heterogeneous surfaces to catalyze many reactions, it also results in less selectivity for heterogeneous processes than for homogeneous processes. Experimentally, this is evident in the large number of products produced in the heterogeneously catalyzed Fischer–Tropsch synthesis. The theoretical foundation for the similarities and differences between heterogeneous and homogeneous catalysis has been illustrated with specific numbers for a particular case.

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Ab Initio Studies on Silicon Compounds. 2.[†] On the Gauche Structure of the Parent Polysilane

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Abstract: Ab initio crystal orbital calculations are performed on the electronic structures of the parent polysilane. We examine the analysis of the energy band structure and the rotational potential in terms of the trans–gauche conformational transitions. We have found that the trans conformer is the ground state of the polysilane. The *gauche*-polysilane (GP) is 0.15 kcal/mol per SiH_2 unit above the *trans*-polysilane (TP). TP has a smaller band gap, lower ionization potential and greater electron delocalization than GP. The effective mass of the hole at the valence band edge is ultimately greater in GP than in TP. All our calculated results suggest that the conservation of near trans conformation is important in the improvement of the semiconductor characteristics of polysilanes.

1. Introduction

Polysilane is a one-dimensional polymer whose backbone consists of only silicon–silicon single bonds. Results of experiments, such as doping with an electron acceptor, photoconduction, and photoluminescence, show that polysilanes are semiconductors.[1] Polysilane is a semiconductive chain with a σ-type skeleton, unlike typical organic semiconductors with π-type frameworks, such as polyacetylene, polypyrrole, polythiophene, and so on. Almost every chemist feels it curious that the σ-electron is so delocalized that it can conduct an electric current. The resonance integrals between two σ-orbitals, however, do not vanish, and a σ-conjugation is possible.[2] We have previously reported some electronic band structure calculations on polysilanes.[3] In the previous calculations, we have naturally assumed the all-trans conformation for polysilanes because the carbon analogue polyethylene is well-known

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