JOURNAL OF CATALYSIS 64, 1-12 (1980)

On Carbon Monoxide Insertion Reactions: A Molecular Orbital Analysis of the Reaction Pathway[1]

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Received March 27, 1979; revised December 13, 1979

A theoretical study of the carbon monoxide insertion reaction in methylmanganese-pentacarbonyl utilizing an all-valence-electron self-consistent-field molecular orbital method in the CNDO approximation is presented. Two possible reaction pathways are analyzed. In one of them the alkyl migration is assumed to be a spontaneous process, while in the other one this migration is accompanied by the entrance of a new CO radical into the coordination sphere of manganese. This allows to evaluate the role played by the latter in promoting the *cis*-migration of the CH_3 group. The present study is in good rapport, from a quantum chemical point of view, with the conclusions previously derived from the exhaustive mechanistic studies for this process.

1. INTRODUCTION

Among catalytic processes, one of the best known reactions is the carbon monoxide insertion into an alkyl–manganese bond. A series of exhaustive mechanistic studies have appeared in the literature (*1*–*9*). Furthermore an extensive review by Calderazzo (*5*) has recently appeared which shows important features of the nature and reactivity of such metal–carbonyl systems.

Nonempirical molecular orbital studies of similar complexes have been reported by Lichtenberger and Brown (*10*). The methyl migration mechanism was not studied by them, but in a recent paper, Berke and Hoffmann (*11*) analyze it using the extended Hückel method in an excellent example of how quantum chemical calculations can provide a coherent picture of the evolution of this class of processes. We shall here present results obtained with a different method which consists of an all-valence-electron self-consistent-field molecular orbital study within the CNDO approximation (*12*). This method has been previously applied to the study of catalytic reactions involving organometallic complexes (*13, 14*). Although the work by Berke and Hoffmann is quite exhaustive (*11*), we believe that a somewhat different approach and the emphasis on other aspects of the reaction here analyzed may supplement their results. Further theoretical studies are in fact underway to obtain fully *ab initio* results, free of the semiempirical approximations inherent in extended Hückel and CNDO calculations, because we believe that it is worthwhile to obtain a good assessment of the quantum picture of this important reaction (*15*).

2. MECHANISTIC STUDIES OF CARBON MONOXIDE INSERTION ON METHYLMANGANESE–PENTACARBONYL

We shall briefly review some of the results of several mechanistic studies that have appeared in the literature. This review is by no means meant to be exhaustive but rather to provide a schematic outline of the experimental information for better comparison with the theoretical results.

The first reports of the methylmanganese–pentacarbonyl system showing the reversible insertion of a CO on the

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[1] Work supported in part by Programa Nacional de Ciencias Básicas, CONACYT.

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0021-9517/80/070001-12$02.00/0

metal–alkyl bond were given by Coffield, Closson and Kozikowski (*1*). Various mechanistic studies for this and related processes, including the use of radioactive ^{14}CO and ^{13}CO species as tracers, have definitely shown that the CO which inserts between the manganese and the organic moiety in the complex does not come from the carbon monoxide present in the reaction atmosphere, but rather is one of the coordinated groups (*2*). Furthermore the question whether the insertion proceeds via a CO insertion movement proper or via *cis*-migration, appears to be in favor of the second alternative (*3*, *4*).

Another important question is the role played by the solvent. Apparently solvent molecules do not participate in the stabilization of the intermediate structure involved in the *cis*-migration (*2*). Also, the geometry of this intermediate structure has been studied, leading to a suggestion that during the *cis*-migration the complex changes from an octahedral hexacoordinated structure to a trigonal–bipyramidal pentacoordinated one (*5*). Infrared spectroscopy studies (*6*, *7*) indicate the possible formation of this last structure.

Perhaps the most important unsettled question concerning the carbonylation reaction in methylmanganese–pentacarbonyl remains whether the coordination of the new CO into the complex is concerted with the *cis*-migration or whether the latter occurs first, being followed by a subsequent addition of carbon monoxide to the coordinatively unsaturated species $CH_3COMn(CO)_4$. Although such an unsaturated complex would presumably by highly energetic, it has also been assumed to exist as an intermediate in the dissociation of acylmanganese–pentacarbonyl (*7*). Furthermore important evidence for the existence of a similar unsaturated trigonal–bipyramidal intermediate in iridium complexes has appeared in the literature (*8*). It should also be mentioned that a similar mechanism for hydride migration in $HMn(CO)_5$ has been proposed by Byers and Brown (*9*).

3. METHOD AND MODELS

All the results reported here were obtained using a modified version of the CNDO/2 program (*12*). The atomic parameters necessary for the calculations are reported in Table 1. The geometrical parameters were taken from the literature (*16*).

Two different reaction coordinates were chosen for the analysis of the migration of the alkyl radical. The first one represents a spontaneous *cis*-migration of CH_3 toward a coordinated CO while the other one represents a "concerted' mechanism (*2*), in which a free CO molecule is allowed to approach the site that the methyl vacates during its movement, thus allowing us to assess the role of the former in activating the movement of the latter.

The difference between these two reaction coordinates lies only in the description of the intermediate stages of the process,

TABLE 1

Atomic Orbital Input Parameters

Element	Atomic Number	Gamma	Orbital exponents			Ionization potentials		
			s	*p*	*d*	*s*	*p*	*d*
Manganese	25	7.95	1.45	0.95	2.93	6.82	3.6	7.93
Carbon	6	15.601	1.55	1.325	—	19.44	10.67	—
Oxygen	8	22.144	2.2	1.975	—	32.38	15.85	—
Hydrogen	1	17.0	1.0	—	—	13.06	—	—

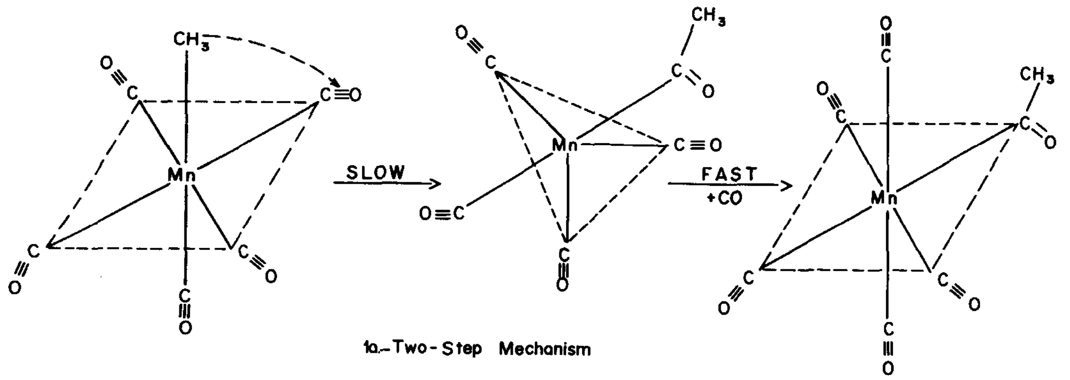
and it is understood that for the first case the entrance of a free CO also takes place, albeit at the second step of the reaction as shown in Fig. 1a. Figure 1b, on the contrary, depicts the other alternative reaction pathway where the free CO is present from the onset. In both cases a sequence of six calculations on the system, representing the corresponding structural changes during the reaction, were carried out. During these six "stages" of the process the relevant bond distances and angles were varied in a linear fashion. For the Fig. 1a case the six stages correspond to the first step only.

4. RESULTS

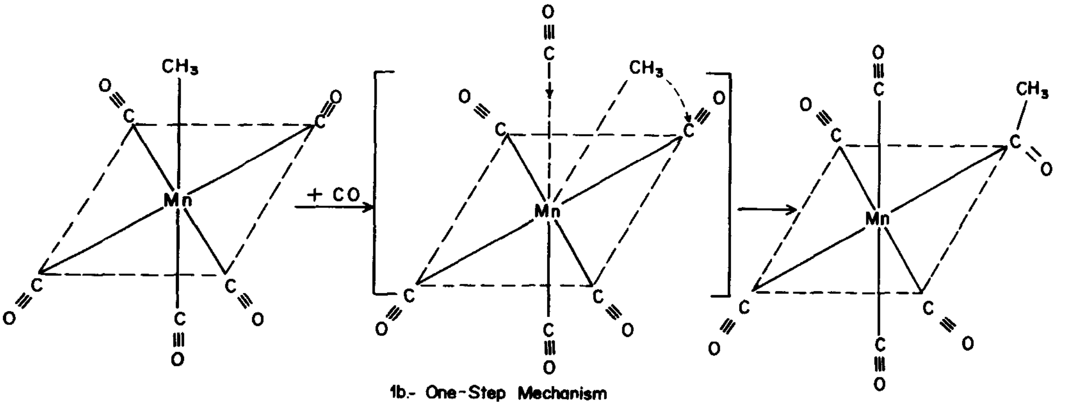
(*a*) *Electronic Structure of the Alkylmanganese-Pentacarbonyl Complex*

The molecular orbital information regarding the alkylmanganese complex is very important to establish the characteristics of the carbonylation reaction. The following molecular orbital ordering in increasing energy was found: $b_2 < e < a_1$, which coincides with previous *ab initio* calculations (*16*) as well as photoelectron spectroscopy (*17*). The separation between the b_2 and e levels is of the order of only 0.01 eV thus implying high concentration of levels of very close energies. The highest occupied molecular orbital (HOMO) is clearly associated with the Mn–methyl σ-bond as shall be shown below. This also was deduced from the Lichtenberger and Fenske experimental results (*17*).

This characteristic of the HOMO has an important bearing in the carbonylation process. It has repeatedly been shown (*14, 15*) in studies of *cis*-migration-type reactions in organometallic complexes that the molecular group whose bond is associ-



1a.-Two-Step Mechanism



1b.- One-Step Mechanism

FIG. 1. Reaction mechanisms for the carbonylation process. (a) The two-step mechanism; (b) the concerted process (one-step mechanism).

ated to the HOMO is the most labile and consequently the most prone to move. This was tested in the present case by relaxing several bond angles in the originally octahedral manganese complex showing that the least impeded movement coresponds to the CH_3 group. The association of the HOMO to the Mn–CH_3 bond shall be more explicitly discussed in the next subsection.

(*b*) *Two-Step Mechanism*

The CH_3 migration coordinate was studied by allowing the methyl to leave its octahedral site and approach a coordinated CO. This movement is represented in a three-dimensional model projected on the plane that contains the manganese, the methyl carbon, and the inserting carbonyl, in Fig. 2. In a sequence of six steps the CH_3

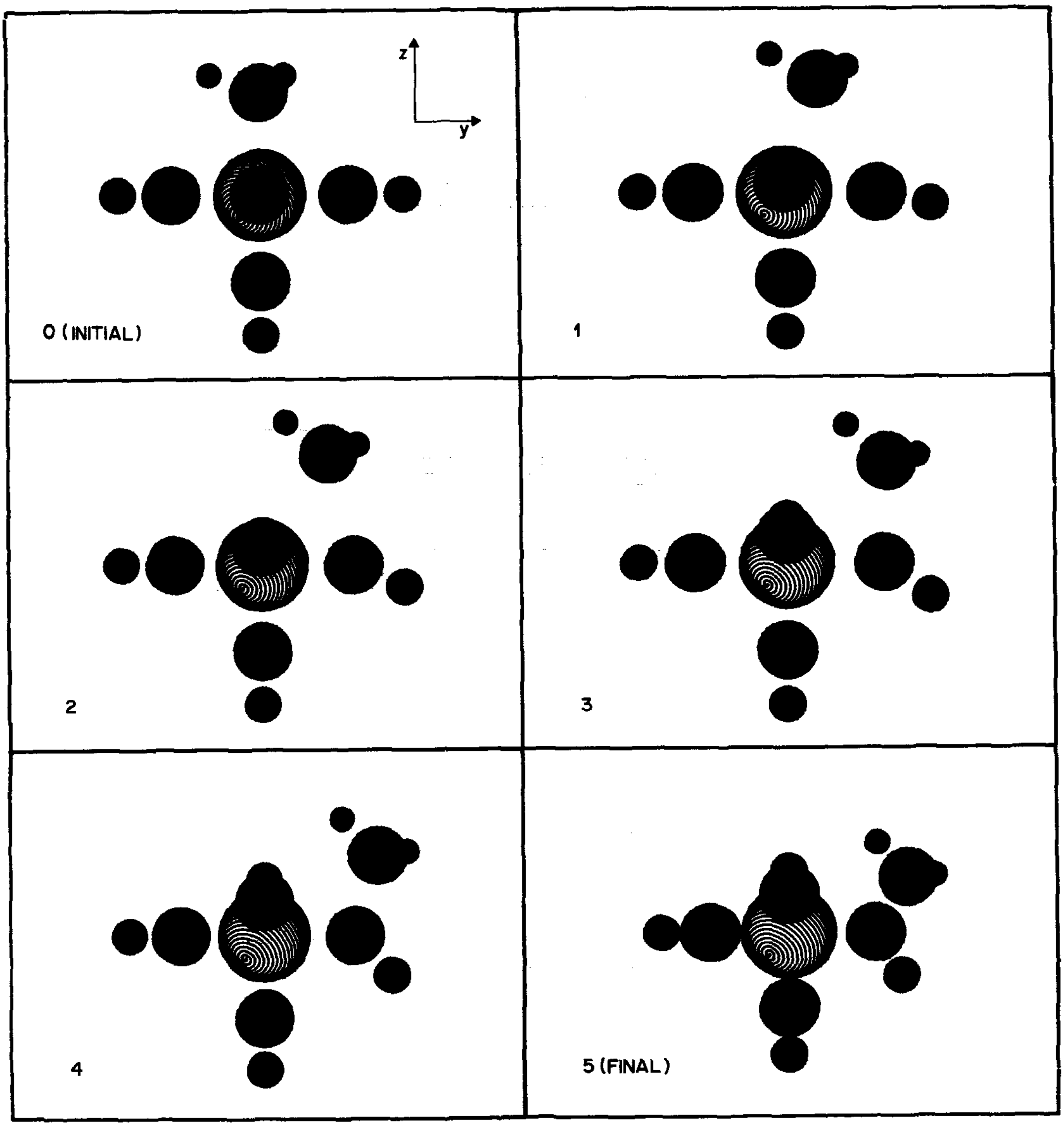


FIG. 2. Illustration of the six stages corresponding to the first step of Fig. 1a. The migration of the CH_3 is viewed from the x-axis.

is viewed as it moves toward CO while both these moieties relax their internal bond angles allowing the formation of an acyl, as is evident in the last stages of Fig. 2. These movements are accompanied by small displacements of other CO moieties not directly involved in the reaction. These movements correspond to the formation of the trigonal–bipyramidal intermediate of Fig. 1a and were included after preliminary calculations, which showed that this intermediate was indeed more favorable than another one maintaining an octahedral symmetry with an unoccupied site left vacant by the methyl displacement. Lichtenberger and Brown (*10*) also report an unsaturated pentacoordinated structure for the fragment Mn(CO)$_4$Br and make a thorough

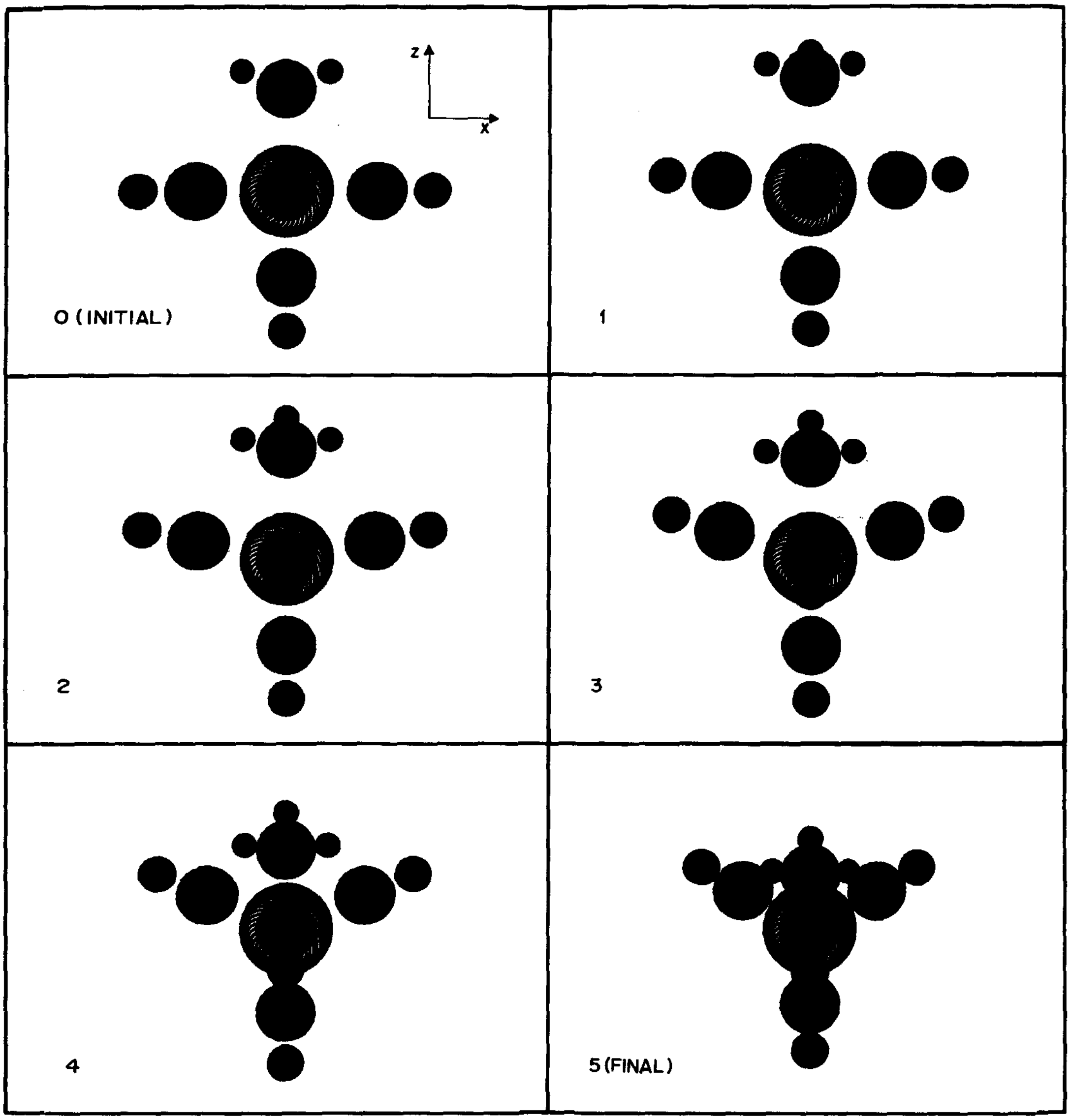


FIG. 3. Relaxation of the coordinated carbonyl groups on the xz plane. This is essentially the same reaction pathway as Fig. 2 but using a different perspective.

study of several geometrical rearrangements which differ very little in energy. In the extended Hückel study (*11*) an intermediate with a geometry described as a "distorted square pyramid" is proposed. In the hydride migration study (*9*), it is proposed that both the square pyramidal and the bipyramidal intermediates can be compatible with the experimental data. This is also in agreement with previous studies on similar *cis*-migration processes on titanium catalysts for which both CNDO (*13*) and *ab initio* (*15*) studies have shown that the undercoordinated complex relaxes to a trigonal–bipyramidal structure. Figure 3, which represents exactly the same reaction stages as Fig. 2 but now observed from a different perspective—the plane of the figure now being perpendicular to the CH_3–Mn bond—shows this structural relaxation toward a trigonal–bipyramid quite clearly.

During the displacements represented in Figs. 2 and 3 the carbonylation proceeds gradually until the formation of the acyl-manganese–tetracarbonyl is achieved. This is clearly evidenced in Fig. 4 where the most relevant bond orders in the manganese complex are depicted as they change through the six successive stages of the reaction coordinate. It is evident that the CH_3 movement debilitates its bond with manganese almost from the onset and finally breaks it, while gradually forming a new C–C bond with the carbonyl moiety. Also notable are the changes in the character of the bonds of the carbon atom in the carbonyl. The C–O bond order reduces from a value of 2.41 to that of a normal double bond (1.96). The corresponding Mn–CO bond order originally identical to those of the other carbonyls acquires more covalent character reaching a value closer to that of an organometallic bond (cf. the final value of the Mn–C bond for the acyl with that of the original alkyl).

Although the total energies obtained by a CNDO calculation are generally unreliable and have shown to be untrustworthy for this type of process (*18*), it is of some interest to note at least the qualitative trends of the evolution of the energy during the process. In Fig. 5 the shape of the activation energy barrier for this reaction coordinate (as well as for the one to be discussed in the following subsection) is depicted. Even disregarding the quantita-

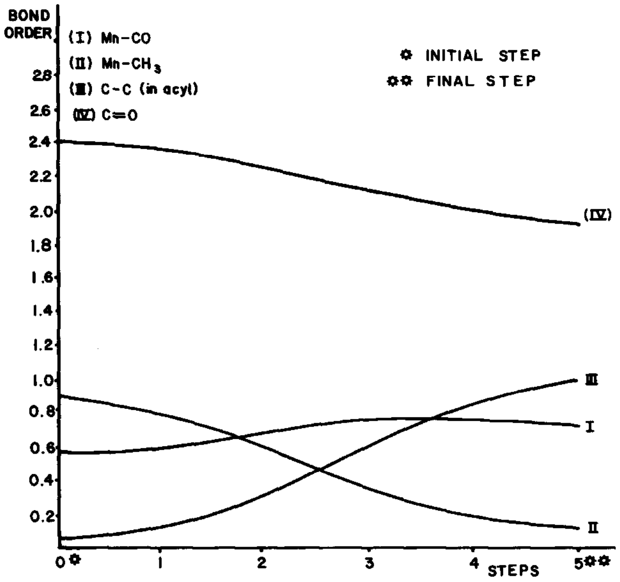


FIG. 4. Evolution of the relevant bond orders during the six stages depicted in Fig. 2.

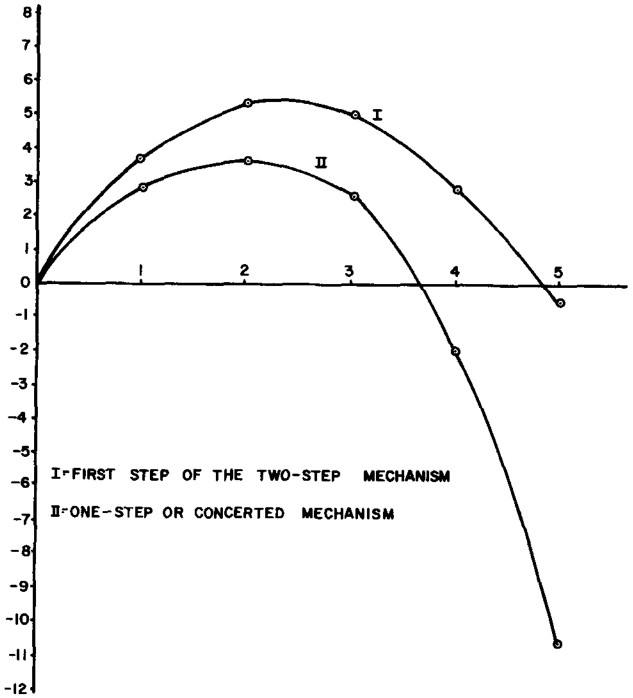


FIG. 5. Total energy evolution for the two reaction pathways of Fig. 1. In order to compare them a common origin is defined wherein the real difference between the two origins would amount to the energy of the extra CO molecule in Fig. 1b. The energy scale is therefore arbitrary.

tive value of the barrier its mere shape shows that the *cis*-migration has to surmount a high barrier confirming the assumption of Calderazzo (*5*) that this coordinatively unsaturated intermediate is not expected to be stabilized. It would also justify the assumption (*3*) that the second step in Fig. 1a (i.e., the coordination of a new carbonyl to manganese) should be very fast to allow the complex to regain its original hexacoordinated status. It should be mentioned that the extended Hückel results (*11*) give an evolution of the energy which is in better agreement with experimental data (they predict an activation barrier of 0.85 eV against the present results of a couple of eV). This stems from a weakness of CNDO energy predictions previously noted for this type of process (*18*). It is of interest, however, even within the present approximations, to compare with other similar systems, because this high barrier lies in marked contrast with the situation found before in other CNDO studies of *cis*-migration in organometallic complexes (*13, 14*). The reason for this difference can be inferred from the analysis of the evolution of the HOMO along the reaction coordinate. In Table 2 the main atomic orbital contributions to the HOMO for the initial methylmanganese–pentacarbonyl complex are given. They are the basis of our statement in the previous subsection that the HOMO essentially corresponds to the Mn–CH_3 bond. In Fig. 6 the main contributions to the HOMO as the reaction proceeds through the six stages of Figs. 2 and 3 are plotted. It is evident that the main contribution from the Mn atom, originally d_{z^2}, gradually incorporates a $d_{x^2-y^2}$ contribution until they reach equivalent value forming a nondirectional bond toward the $COCH_3$ group. In Table 2, in fact, the contributions to the HOMO for the acetylmanganese–tetracarbonyl intermediate are also reported showing that the

TABLE 2

Dominant Contributions to the HOMO during the Process of Fig. 2

Step	Orbital	Most relevant coefficients to HOMO
Initial	−6.7500	$-0.61\, d_{z^2}$ (Mn) $+ 0.66\, p_z$ (C[a])
1	−6.2212	$-0.60\, d_{z^2}$ (Mn) $+ 0.63\, p_z$ (C[a])
2	−5.8911	$-0.61\, d_{z^2}$ (Mn) $+ 0.56\, p_z$ (C[a])
3	−5.8625	$-0.58\, d_{z^2}$ (Mn) $+ 0.43\, p_z$ (C[a]) $+ 0.29\, p_y$ (C[b])
4	−5.9283	$-0.40\, d_{x^2-y^2}$ (Mn) $- 0.52\, d_{z^2}$ (Mn) $+ 0.29\, p_z$ (C[a]) $+ 0.38\, p_y$ (C[b])
Final	−5.8532	$-0.47\, d_{x^2-y^2}$ (Mn) $- 0.48\, d_{z^2}$ (Mn) $+ 0.42\, p_y$ (C[b]) $- 0.39\, p_y$ (O[c])

[a] Carbon of CH_3.
[b] Carbon of the CO that reacts with CH_3.
[c] Oxygen of the CO that reacts with CH_3.

HOMO now is basically associated with the metal–acetyl bond. The fact that this bond is not strictly directed to the first carbon atom on the acetyl but also interacts with the other one may well favor the dissociation mechanism of the acetyl, i.e., the reverse process of Fig. 1a.

The main difference with previous

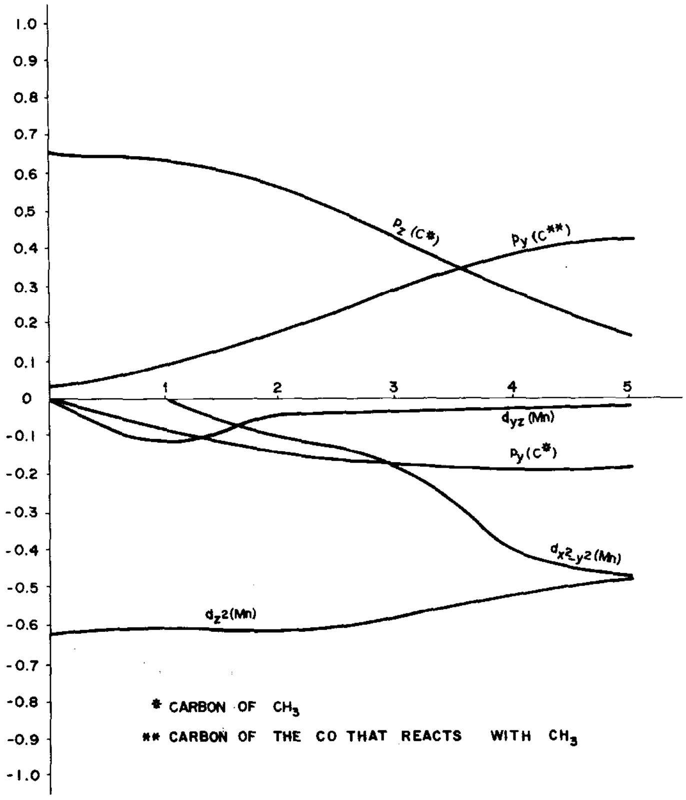


FIG. 6. Dominant contributions to the HOMO during the process of Fig. 2.

studies on the Ziegler–Natta process (*13, 18*), for instance, lies in the fact that there is no empty *d*-orbital in Mn (as there is in Ti) that can act as a carrier of the Mn–CH_3 bond when the CH_3 displacement begins. In our coordinate system convention the natural candidate would be d_{yz}. From Fig. 6 however it is seen that after a weak contribution at stage 1 of the process d_{yz} fades away from the HOMO. This may also be inferred from the CNDO density matrix. In Table 3 the values of the density for all *d*-orbitals in manganese are shown. Obviously d_{xy}, d_{xz}, and d_{yz} are doubly occupied throughout the reaction thus receding into the Mn atom and playing little role in bond formation. Originally d_{z^2} has a population of about one e^- and $d_{x^2-y^2}$ about half of that value while at the final structure their combined population is again about one and one-half, respectively, but they now have almost identical densities due to the above-discussed nondirectional aspect of the metal–acyl bond. These are the only *d*-orbitals available for bond formation at the Mn site and, at the intermediate stages, the CH_3 movement implies a much higher barrier than in the case of Ti with its empty *d*-orbitals (*13*).

TABLE 3

Electronic Population for the Mn *d*-Orbitals through the Reaction Coordinates of the Two-Step and One-Step Mechanisms

	Electronic population (density matrix)				
	$d_{x^2-y^2}$	d_{xz}	d_{z^2}	d_{yz}	d_{xy}
Two-step mechanism					
Initial	0.444	1.923	0.987	1.923	1.890
1	0.442	1.918	0.936	1.882	1.898
2	0.445	1.917	0.966	1.828	1.907
3	0.552	1.918	0.919	1.793	1.912
4	0.669	1.919	0.795	1.796	1.917
Final	0.734	1.920	0.720	1.805	1.922
Concerted mechanism					
Initial	0.441	1.927	0.978	1.927	1.890
1	0.442	1.885	0.981	1.895	1.892
2	0.492	1.865	0.986	1.870	1.863
3	0.683	1.905	0.810	1.869	1.822
4	0.811	1.918	0.680	1.897	1.870
Final	0.983	1.889	0.688	1.908	1.923

(*c*) *One-Step Mechanism*

We shall now present the reaction pathway associated with the process depicted in Fig. 1b, i.e., the concerted entrance from the reaction medium of a free CO into the coordination sphere while the methyl undergoes its *cis*-migration. The representation of the six successive stages with which we modeled the reaction appears in Fig. 7. The approach toward Mn of the new CO starts at 6 Å from the complex and gradually advances (1 Å at each of the earlier stages and 0.5 Å at the two last ones) until it reaches a position equivalent to the other coordinated CO moieties. The bond orders during the pathway are reported in Fig. 8. Comparing with Fig. 4 we see that all the bond orders involved with the *cis*-migration have virtually identical evolution in both reactions. Furthermore the entrance of the free CO simply forms a new Mn–CO bond but hardly interacts with the migrating CH_3, for instance. This is well-known experimentally—the CH_3 is never carbonylated by molecules coming from the reaction atmosphere (*1*). The negligible bond order between these moieties (too small to appear in Fig. 8) throughout the reaction pathway merely reflects this fact at a molecular orbital level.

From the analysis of the HOMO we again find that the interactions take place between the same atomic orbitals described in the previous subsection, that is, those that shall form the acetyl–manganese bond. The entering CO does not participate in this molecular orbital, in spite of the fact that the HOMO is originally formed from the Mn d_{z^2} and p_z, i.e., it is directed exactly toward the incoming CO. The latter's contribution to the HOMO, however, is negligible throughout the whole process. When the free CO starts to interact with the Mn coordination sphere in fact, it immediately acquires a character similar to the other coördinated carbonyls, its bond being located in low-lying molecular orbitals. If we consider the fact that the methyl–carbon

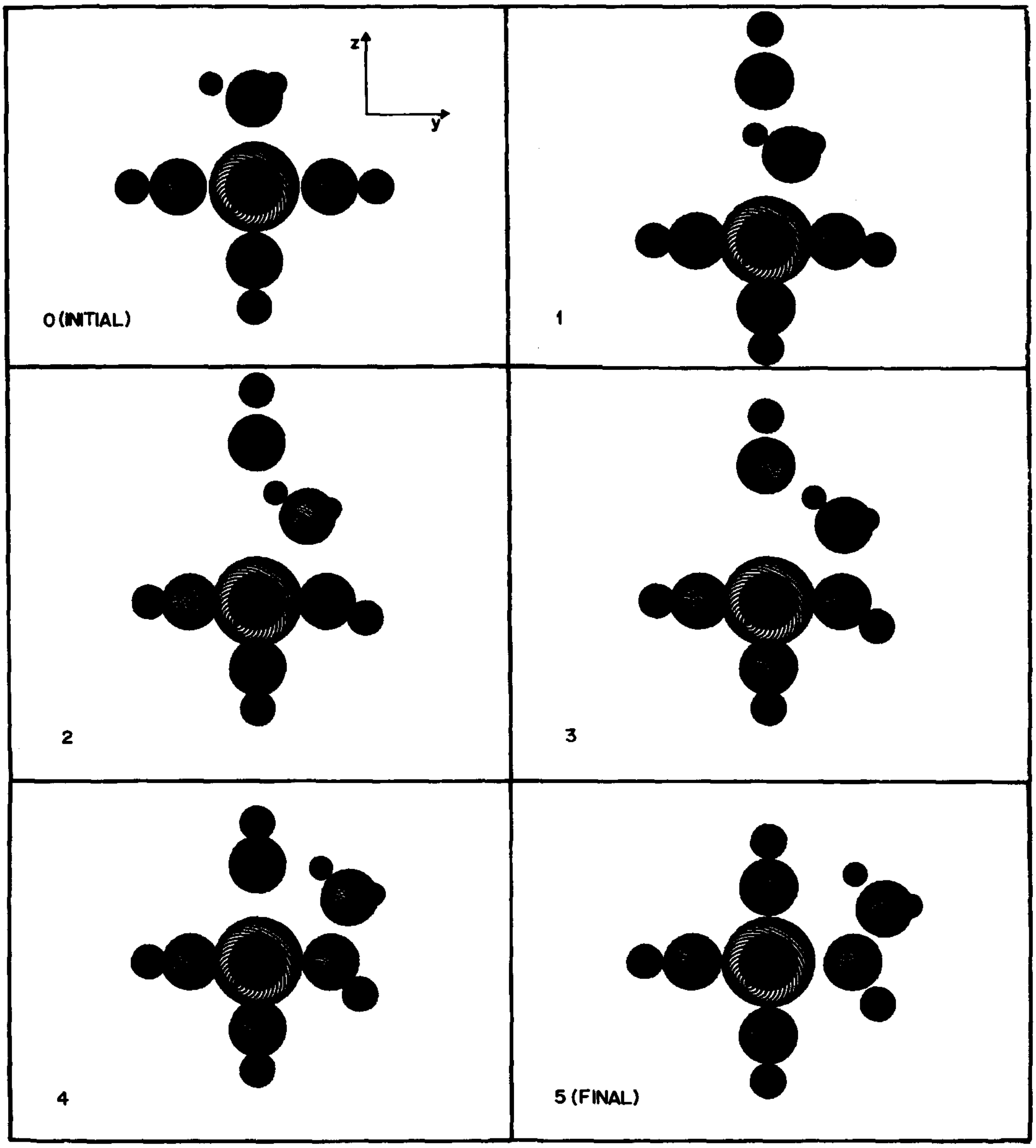


FIG. 7. Illustration of the concerted mechanism (one-step process in Fig. 1b), in which the entrance of the free CO simultaneously to the formation of the acetyl is appreciated.

distance with respect to the incoming CO carbon during the earlier stages is not much longer than its distance to the coordinated CO carbon (2.8 Å vs 2.6 Å at stage 2, for instance, and yet the corresponding bond orders are 0.03 and 0.21, respectively), we see that the quantum chemical picture fully supports the assumption that the carbonylation can occur only with coordinated CO moieties. Furthermore the role of the Mn in facilitating the reaction is evident as the coordinated CH_3 and CO carbons interact mainly through the Mn *d*-functions as our HOMO analysis has shown.

The question whether the entrance of a free CO actually promotes the reaction has

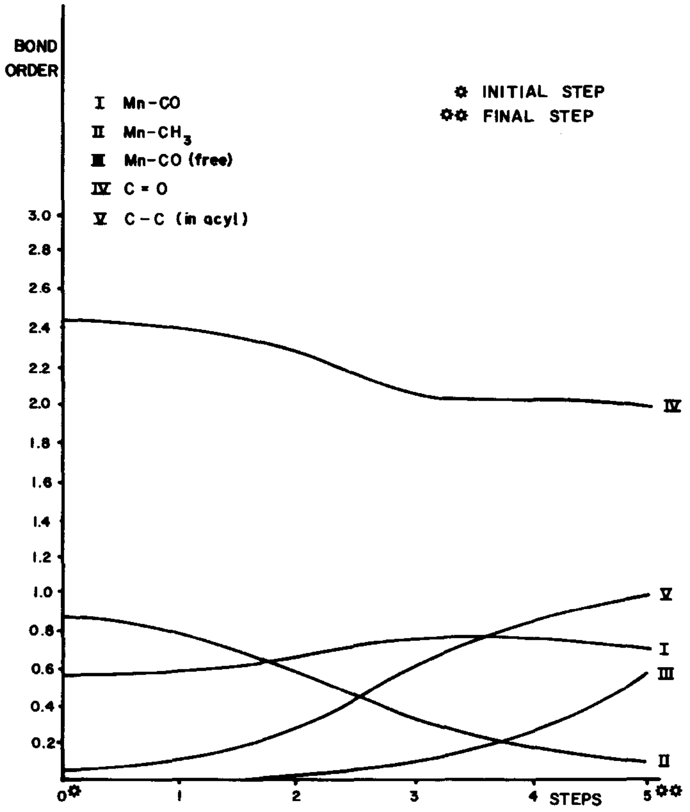


FIG. 8. Evolution of the relevant bond orders during the concerted process of Fig. 7.

not been answered unequivocally (*5*) from mechanistic studies. Theoretically it is also hard to decide whether the entrance of the CO can activate the methyl migration. The evolution of the energy both for the two-step and the one-step process are depicted in Fig. 5. Evidently the entrance of an extra CO molecule plays an enormous role in stabilizing the Mn complex. One must remember, however, that the two-step process is described up to the formation of the acetylmanganese–tetracarbonyl, which is not the final product of the reaction of Fig. 1a but a labile intermediate. Thus the formation of a new Mn–CO bond to saturate the manganese coordination must also be assumed for the two-step process, as a second step that follows the methyl migration, and the final energy will go down correspondingly. At the earlier stages of both reactions (see Fig. 5) the energy goes up steeply, and even if the activation barrier is one-third lower in the case where the extra CO is present, it is still quite high. In spite of the fact that CNDO calculations can ony provide qualitative predictions in this respect, we find no evidence in our results to point out that the presence of a molecule from the reaction medium is necessary to promote (*2*) the *cis*-migration reaction. It is interesting to comment that Berke and Hoffmann (*11*) also found that the incoming ligand actually does not play a relevant role in the early steps of the reaction and only stabilizes the organometallic complex until the last stages of the process.

5. OUTLOOK AND PERSPECTIVE

The all-valence-electron semiempirical results here reported have allowed us to analyze the carbonylation process from a molecular orbital point of view. Several questions, previously studied experimentally, can also be approached theoretically, such as the preferred migration of the CH_3 over the CO, the fact that the reaction involves a coordinated carbonyl and not a carbonyl coming from the reacting medium, the stabilization of a trigonal–bipyramidal intermediate, etc. Furthermore new insight is added on these aspects when they are analyzed from a more fundamental standpoint, based in the electronic distribution of the reacting system. Again we must remark that the present results supplement those of Ref. (*11*) in which some of these questions were first studied at a molecular orbital level.

However, many questions remain open. Especially important is the possibility of obtaining reliable energy changes that permit a unique prediction of how the process can evolve. To obtain such quantum chemical results—quantitatively trustworthy and free of the parameterization involved in semiempirical methods—*ab initio* studies both at the all-valence-electron level (using the pseudo-potential method of Barthelat, Durand, and Serafini (*19*)) and the all-electron-molecular-orbital SCF method for the same process (*15*) are being carried out.

ACKNOWLEDGMENTS

We are grateful to Professors Jack Halpern, Theodore Brown, and Fausto Calderazzo for interesting comments concerning the carbon monoxide insertion reaction. We also acknowledge the help of the computing division at Instituto Mexicano del Petróleo and especially the use of the program developed by Professor H. V. McIntosh for the plots in Figs. 2, 3, and 7.

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