

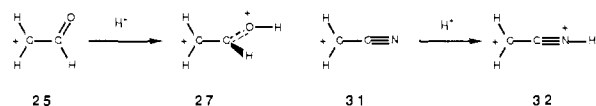
Table IV. Total Energies (au) for Ions 14-22

ion	STO-3G//STO-3G	4-31G//STO-3G
14	-376.876 71	-381.031 73
15	-376.871 92	-381.027 89
16	-356.188 52	-360.067 46
17	-377.088 68	-381.183 48
18	-377.097 12	-381.193 61
19	-377.091 79	-381.186 52
20	-356.389 33	-360.233 66
21	-303.161 38	-306.379 21
22	-303.181 94	-306.399 89

Table V. Total Energies (au) for Ions 25-34

ion	STO-3G//STO-3G	4-31G//4-31G	6-31G**//4-31G
25	-150.023 33	-151.711 61	-151.941 82
26	-150.010 54	-151.704 94	-151.940 41
27	-150.129 20	-151.784 37	-152.014 15
28	-150.105 47	-150.769 15	-151.999 82
29	-150.122 25	-151.773 90	-152.005 12
30	-150.105 47	-151.756 90	-151.989 28
31	-129.324 37	-130.748 45	-130.942 31
32	-129.399 18	-130.808 44	-130.999 10
33		-226.565 07	-226.910 87
34		-226.559 13	-226.905 62

dication 27, was 45.4 kcal/mol (6-31G\*\*//4-31G), and that of the CN-substituted ion 31 to 32 was 35.6 kcal/mol (6-31G\*\*//4-31G). The larger proton affinity of 25 (by 9.76 kcal/mol) provided a theoretical interpretation for the experimental substituent effects of carbonyl and cyano groups in the reactions of the diphenylmethyl cations in a strong acid.



### Conclusion

The STO-3G calculations showed that, although  $\pi$ -electron-withdrawing substitutions such as CHO and CN groups on the

carbenium center of the benzyl cation have no effect on the charge distributions or on the frontier orbital coefficients, relative to the parent benzyl cation, the protonation on the substituents acquired the ethylene dication character, which repels the positive charge and substantially delocalizes it over the aromatic ring. The charge distributions over the aromatic ring are comparable with those of phenylnitrenium ion and phenoxenium ion. The higher level calculations on the simple substituted ethylene dications revealed that a perpendicular structure of ethylene dication is favored over the planar one. The CHO group conjugating with the carbenium center is more basic than the CN group in a similar system. These results are consistent with the experimental observations on the reactions of diphenylmethyl cations in a strong acid.

### Experimental Section

**Calculation Methods.** The calculations have been performed at the Computer Center of the University of Tokyo. The ab initio calculations were carried out by using a modified version of the GAUSSIAN 80 computer programs (GAUSSIAN 80H).<sup>16</sup> Structures of cations (benzyl cation 13, phenylnitrenium ion (23) and phenoxenium ion (24)) were completely optimized by using Marataugh-Sargent gradient optimization techniques and the split-valence RHF/4-31G basis set with the constraints of planar symmetry and  $C_2$  symmetries (except 23). The  $\alpha$ -substituted benzyl cations 14-22 were optimized on the minimal STO-3G level, and single-point calculations on the 4-31G basis set for the STO-3G-optimized geometries were performed because of the limited number of the allowed primitive shell functions on this Gaussian version. Total energies of these ions 14-22 are given in Table IV. The complete optimizations on simple substituted methyl cations and substituted ethylene dications 25-34 were carried out on both STO-3G and 4-31G basis sets. To estimate the energetics accurately, single-point calculations on 4-31G-optimized geometries were also performed at d-polarized 6-31G\*. Total energies of these ions 25-34 are given in Table V.

**Acknowledgment.** We thank Dr. A. Itai, Y. Toriumi, and Dr. N. Tomioka, Faculty of Pharmaceutical Sciences, University of Tokyo, for their helpful advice and for the use of their calculation systems.

**Registry No.** 13, 6711-19-9; 14, 117687-20-4; 16, 65108-03-4; 17, 117687-21-5; 20, 117687-22-6; 21, 117687-23-7; 23, 117687-27-1; 24, 77417-34-6; 25, 41084-88-2; 27, 117687-24-8; 31, 34430-18-7; 32, 117687-25-9; 33, 117687-26-0.

## Molecular Analogues of Surface Species. 2.<sup>†</sup> A Theoretical Study of Molybdenum Carbonyl Thiophene Complexes: Organometallic Models for the Chemisorption of Thiophene

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**Abstract:** Molecular orbital (CNDO) calculations on the interaction of  $\text{Mo}(\text{CO})_n$  ( $n = 3, 5$ ) fragments with thiophene suggest that formation of the hitherto unknown complexes  $\text{Mo}(\eta^1\text{S-thiophene})(\text{CO})_5$  and  $\text{Mo}(\eta^5\text{-thiophene})(\text{CO})_3$  is possible. The nature of the thiophene-metal bond is mainly  $sp-sp$  with some  $d-d$  and  $sp-d$  contributions. Thiophene is more strongly bound in the  $\eta^5$  than in the  $\eta^1\text{S}$  complex, and activation of the C-S bonds toward nucleophilic attack at the  $\alpha$ -carbons is expected in the former case but not in the latter. This theoretical approach leads to conclusions which agree well with experimental organometallic and surface chemistry results.

The hydrodesulfurization (HDS) reaction is of prime importance in the petroleum industry. Despite this industrial impact and numerous studies devoted to this process, a fundamental understanding of the catalytic sites, reaction intermediates, and elementary steps of the HDS process is far from complete.<sup>1</sup> The most widely used catalysts are composed of molybdenum or tungsten sulfides supported on alumina and promoted by cobalt

or nickel. Many other metal sulfides in bulk or dispersed on a support have also proved to be active in HDS.<sup>2</sup>

(1) (a) Gates, B. C.; Katzer, J. R.; Schuit, G. C. A. *Chemistry of Catalytic Processes*; McGraw-Hill: New York, 1979. (b) Satterfield, C. N. *Heterogeneous Catalysis in Practice*; McGraw-Hill: New York, 1980. (c) Grange, P. *Catal. Rev. Sci. Eng.* 1977, 15, 249. (d) Schuman, S. C.; Shalit, H. *Catal. Rev.* 1970, 4, 245. (e) Mitchell, P. C. H. *Catal. (London)* 1977, 1, 204 and 1981, 4, 175. (f) Kwart, H.; Schuit, G. C. A.; Gates, B. C. *J. Catal.* 1980, 61, 128.

<sup>†</sup>Reference 12 is to be considered part 1 of this series.

Because of the extreme complexity of the chemistry involved in petroleum hydrotreatment, mechanistic studies frequently use thiophene as a model compound for petroleum constituents. A key step in the reaction mechanism in this case is the chemisorption of thiophene on metal sites of the catalyst; however, the detailed nature of the intermediate containing the adsorbed thiophene remains unclear. On the basis of kinetic evidence adsorption through the sulfur atom ( $\eta^1$ S-bonding),<sup>3</sup> a C=C bond ( $\eta^2$ -bonding),<sup>1f,4</sup> the diene system ( $\eta^4$ -bonding), or the whole  $\pi$ -electron system ( $\eta^5$ -bonding)<sup>5</sup> have been proposed. Surface techniques<sup>6-10</sup> as well as theoretical calculations<sup>11</sup> have also provided evidence for the same four types of bonding. Recent studies by Zaera et al.<sup>6a</sup> and by Roberts and Friend<sup>8</sup> on the thermal decomposition of thiophene over Mo(100) and Mo(110) single crystal surfaces, respectively, show that thiophene can be adsorbed perpendicular as well as parallel to the surface. Blake et al.<sup>9</sup> detected thiophene chemisorbed onto a MoS<sub>2</sub> catalyst in a vertical manner by NMR spectroscopy, which is consistent with the results of Kelly et al.<sup>10</sup> on a clean Mo(100) surface. An alternative approach used by ourselves<sup>12</sup> and others<sup>13,14</sup> which may provide additional information toward the understanding of thiophene chemisorption is the synthesis of discrete metal-thiophene complexes amenable to characterization at the molecular level. A number of examples of such complexes are available in the literature. Both the  $\eta^1$ S and the  $\eta^5$  bonding modes have been identified or proposed; other types of bonding such as  $\eta^2$  or  $\eta^4$ , although chemically reasonable, have hitherto never been observed.

$\eta^1$ S-bonded complexes of thiophene are limited to iron,<sup>15</sup> which is a poorly active metal in HDS,<sup>2</sup> and ruthenium,<sup>13a,16</sup> which is one of the most active HDS metals.<sup>2</sup> In the latter case, however, the complexes are rather unstable and consequently not well characterized.<sup>13a,16</sup> Stable ruthenium complexes have been obtained by attaching the thiophene ring to more complex ligand systems

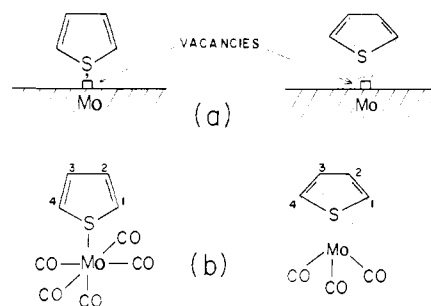


Figure 1. Models of thiophene adsorption: (a) on surfaces that contain molybdenum and (b) on molybdenum complex fragments.

Table I. Atomic Parameters

atom		Slater exponent	$(I + A)/2$ (eV)	Beta (eV)
Mo <sup>a,b</sup>	s	1.40	3.93	7.50 <sup>a</sup>
	p	1.40	0.71	7.50 <sup>a</sup>
	d	2.40	4.53	11.50 <sup>a</sup>
S <sup>c</sup>	s	1.82	17.65	18.15
	p	1.82	6.99	18.15
	d	1.82	0.71	18.15

<sup>a</sup>This work. <sup>b</sup>Reference 11a. <sup>c</sup>Reference 29.

containing strongly coordinating groups such as phosphine<sup>13b</sup> or cyclopentadienyl,<sup>13a</sup> and in such cases Ru-S bonding could be clearly established by X-ray diffraction.

$\eta^5$ -Bonding, on the other hand, has been found for Cr,<sup>17</sup> Mn,<sup>14a,b,18</sup> Fe,<sup>15c,19</sup> Ru,<sup>12,14f,20</sup> Rh,<sup>12,14f,20</sup> and Ir,<sup>12,14f,20</sup> and the complexes appear to be generally more stable than the  $\eta^1$ S-derivatives. The only X-ray structures reported for  $\eta^5$ -thiophene complexes are those of [Rh( $\eta^5$ -thiophene)(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup><sup>12</sup> (one of the most highly active HDS metals)<sup>2</sup> and Cr( $\eta^5$ -thiophene)(CO)<sub>3</sub><sup>17b</sup> (a poorly active HDS metal).<sup>2</sup> No thiophene complexes of molybdenum are known at present, and our own efforts toward the synthesis of Mo(CO)<sub>5</sub>( $\eta^1$ -thiophene) or Mo(CO)<sub>3</sub>( $\eta^5$ -thiophene) from Mo(CO)<sub>6</sub> or derivatives thereof have so far met with no success. This is somewhat surprising, since one of the earliest and best characterized thiophene complexes is the analogous Cr(CO)<sub>3</sub>( $\eta^5$ -thiophene).<sup>17</sup>

There are, to our knowledge, no reported theoretical investigations concerning metal-thiophene complexes. This paper describes the interaction of Mo(CO)<sub>5</sub> and Mo(CO)<sub>3</sub> fragments with thiophene to form Mo(CO)<sub>5</sub>( $\eta^1$ S-thiophene) and Mo(CO)<sub>3</sub>( $\eta^5$ -thiophene) complexes.

### Computational Details

The theoretical method used here is the CNDO-UHF from GEOMO program<sup>21</sup> with corrections suggested in the literature<sup>22</sup> and modifications carried out to improve the performance of the calculations.<sup>23,24</sup> In this work, we do not perform an exhaustive search for atomic parameters as was done in previous publications.<sup>23,24</sup> Here, we are more interested in a qualitative study similar to Hoffmann's work<sup>25,26</sup> for other transition-metal complexes. The  $\beta$  parameters for molybdenum were adjusted in order to get a good correlation with the dissociation bond energy of the Mo-O diatomic molecule<sup>27</sup> at the average experimental bond distance of 1.67 Å.<sup>28</sup> The  $(I + A)/2$  quantities and the screening atomic pa-

(2) (a) Pecoraro, T. A.; Chianelli, R. R. *J. Catal.* **1981**, *67*, 430. (b) Harris, S.; Chianelli, R. R. *J. Catal.* **1987**, *86*, 400. (c) Chianelli, R. R. *Catal. Rev. Sci. Eng.* **1984**, *26*, 361. (d) Harris, S. *Polyhedron* **1986**, *5*, 151. (e) Vissers, J. P. R.; Groot, C. K.; Van Oers, E. M.; De Beer, V. H. J.; Prins, R. *Bull. Soc. Chim. Belg.* **1984**, *93*, 813. (f) Ledoux, M. J.; Michaux, O.; Agostini, G.; Panissod, P. *J. Catal.* **1986**, *102*, 275.

(3) (a) Lipsch, J. M. J. G.; Schuit, G. C. A. *J. Catal.* **1969**, *15*, 179. (b) Kolboe, S. *Can. J. Chem.* **1969**, *47*, 352. (c) Duben, A. J. *J. Phys. Chem.* **1978**, *82*, 348.

(4) Griffith, R. H.; Marsh, J. D. F.; Newling, W. B. S. *Proc. R. Soc. (London), Ser. A* **1949**, *197*, 194.

(5) (a) Smith, G. V.; Hinckley, C. C.; Behbahany, F. *J. Catal.* **1973**, *30*, 218. (b) Zdrzil, M. *Collect. Czech. Chem. Commun.* **1977**, *42*, 1484. (c) Cowley, S. W. Ph. D. Thesis, Southern Illinois University, Carbondale, IL, 1975.

(6) (a) Zaera, F.; Kollin, E. B.; Gland, G. J. L. *Surf. Sci.* **1987**, *184*, 75 and references therein. (b) Zaera, F.; Kollin, E. B.; Gland, J. L. *Langmuir* **1987**, *3*, 555 and references therein.

(7) (a) Schoofs, G. R.; Preston, R. E.; Benziger, J. B. *Langmuir* **1985**, *1*, 313 and references therein. (b) Blyholder, G.; Bowen, D. O. *J. Phys. Chem.* **1962**, *66*, 1288. (c) Nicholson, D. E. *Anal. Chem.* **1962**, *34*, 370.

(8) Roberts, J. T.; Friend, C. M. *Surf. Sci.* **1987**, *186*, 201.

(9) Blake, M. R.; Eyre, M.; Moyes, R. B.; Wells, P. B. *Proceedings of the 7th International Congress on Catalysis* Seiyama, T., Tanabe, K., Eds.; Elsevier: Tokyo, 1980; Vol. 7, Part A, p 591.

(10) Kelly, D. G.; Salmeron, M.; Somorjai, G. A. *Surf. Sci.* **1986**, *175*, 465.

(11) (a) Ruetter, F.; Ludeña, E. V. *J. Catal.* **1981**, *67*, 266. (b) Joffre, J.; Lerner, D. A.; Geneste, P. *Bull. Soc. Chim. Belg.* **1984**, *93*, 831. (c) Joffre, J.; Geneste, P.; Lerner, D. A. *J. Catal.* **1986**, *97*, 543.

(12) Sanchez-Delgado, R. A.; Marquez-Silva, R. L.; Puga, J.; Tiripicchio, A.; Tiripicchio-Camellini, M. *J. Organomet. Chem.* **1986**, *316*, C35.

(13) (a) Draganjac, M.; Ruffing, C. J.; Rauchfuss, T. B. *Organometallics* **1985**, *4*, 1909. (b) Bucknor, S. M.; Draganjac, M.; Rauchfuss, R. B.; Ruffing, C. J.; Fultz, W. C.; Rheingold, A. L. *J. Am. Chem. Soc.* **1984**, *106*, 5379.

(14) (a) Lesch, D. A.; Richardson, J. W.; Jacobson, R. A.; Angelici, R. J. *J. Am. Chem. Soc.* **1984**, *106*, 2901. (b) Hockett, S. C.; Sauer, N. N.; Angelici, R. J. *Organometallics* **1987**, *6*, 591. (c) Spies, G. H.; Angelici, R. J. *J. Am. Chem. Soc.* **1985**, *107*, 5569. (d) Spies, G. H.; Angelici, R. J. *Organometallics* **1987**, *6*, 1897. (e) Saver, N. N.; Angelici, R. J. *Organometallics* **1987**, *6*, 1146. (f) Hockett, S. C.; Miller, L. L.; Jacobson, R. A.; Angelici, R. J. *Organometallics* **1988**, *7*, 686.

(15) (a) Kuhn, N.; Schumann, H. *J. Organomet. Chem.* **1984**, *276*, 55. (b) Catheline, D.; Astruc, D. *J. Organomet. Chem.* **1983**, *248*, C9. (c) Guerchais, V.; Astruc, D. *J. Organomet. Chem.* **1986**, *316*, 335.

(16) Kuehn, C. G.; Taube, H. *J. Am. Chem. Soc.* **1976**, *98*, 689.

(17) (a) Fischer, E. O.; Ofele, K. *Chem. Ber.* **1958**, *91*, 2395. (b) Bailey, M. F.; Dahl, L. F. *Inorg. Chem.* **1965**, *4*, 1306.

(18) Singer, H. *J. Organomet. Chem.* **1967**, *9*, 135.

(19) (a) Lee, C. C.; Iqbal, M.; Gill, U. S.; Sutherland, R. G. *J. Organomet. Chem.* **1985**, *288*, 89. (b) Braitsch, D. M.; Kumarappan, R. *J. Organomet. Chem.* **1975**, *84*, C37.

(20) Russell, M. J. H.; White, C.; Yates, A.; Maitlis, P. M. *J. Chem. Soc., Dalton. Trans.* **1978**, 857.

(21) Rinaldi, D. GEOMO Program, QCPE, No. 290.

(22) Mayer, I.; Révész, M. *Comput. Chem.* **1982**, *6*, 153.

(23) Hernández, A. J.; Ruetter, F.; Ludeña, E. V. *J. Mol. Catal.* **1987**, *39*, 21.

(24) Castejón, H.; Hernández, A. J.; Ruetter, F. *J. Phys. Chem.*, in press.

(25) Hoffmann, R. *Science (Washington, D.C.)* **1981**, *211*, 995.

(26) Saillard, J. Y.; Hoffmann, R. *J. Am. Chem. Soc.* **1984**, *106*, 2006.

(27) Rosen, B. *Spectroscopy Data Relative to Diatomic Molecules*; Pergamon Press: New York, 1970.

(28) Schroder, F. A. *Acta Crystallogr.* **1975**, *B31*, 2294.

parameters were obtained from previous calculations on molybdenum-thiophene systems.<sup>11a</sup> The molybdenum and sulfur parameters are summarized in Table 1. The C, O, and H are the standard ones given by Pople and Beveridge.<sup>29</sup> The d orbitals were included for the sulfur atom because it is known that they play an important role in the electronic properties of sulfur-containing compounds.<sup>30,31</sup>

Geometries for the  $\eta^1$  and  $\eta^5$  complexes and for the  $\text{Mo}(\text{CO})_5$  and  $\text{Mo}(\text{CO})_3$  fragments were adopted from the crystal structure of  $\text{Mo}(\text{C}-\text{O})_6$ .<sup>32</sup> We used the coordinates of Harshbrager and Bauer<sup>33</sup> for the thiophene molecule.

All these calculations were performed by considering only the optimization of the thiophene- $\text{ML}_n$  fragment distance leaving the other internuclear distances fixed. Therefore, the restriction of not allowing relaxation of the thiophenic and  $\text{Mo}-\text{C}-\text{O}$  bonds and the fact that the parametrization was not rigorous give these calculations a qualitative character.

## Results and Discussion

**1. Metal Complexes as Models for Surface Species.** The homogeneous (solution) chemistry of discrete metal complexes has provided interesting mechanistic models for heterogeneously catalyzed processes.<sup>34</sup> Also, theoretical calculations on molecular complexes have been used to interpret the chemistry of surfaces.<sup>26,35</sup>

A coordinatively unsaturated transition-metal fragment  $\text{ML}_n$  ( $M = \text{metal}$ ,  $L = \text{ligand}$ ) simulates a surface adsorption site where a reactive molecule (adsorbate) is chemisorbed. A prototype of such a fragment is that obtained by subtracting some CO ligands from a metal-carbonyl complex,  $\text{M}(\text{CO})_n$ . These fragments have been proposed as intermediates in reactions of metal-carbonyl complexes<sup>36</sup> and have been detected by matrix isolation techniques.<sup>36,37</sup> One can envisage such fragments as molecular analogues of adsorption sites on solid catalysts (known as vacancies), where surface coordination bonds are incomplete.

Because chemisorption can be considered a local phenomenon, only a few atoms are necessary in principle to simulate an adsorption site. Thus, the concept of using organometallic fragments and complexes as molecular analogues of surface sites and intermediates is justified. As in all models, however, we recognize some limitations, especially where mononuclear complexes are involved. Chemisorption can occur in multicenter adsorption sites, and neighboring metallic atom participation could be of great importance in subsequent steps of the catalytic process. On the other hand, fragments and complexes offer the advantageous possibility of varying the number and the nature of the ligands, thereby allowing the study of the influence of oxidation states, coordinative unsaturation, and the electronic role of promoters in the first step of catalytic reactions, i.e., chemisorption.

This organometallic approach has only recently been applied to the HDS reaction, through the synthesis and reactivity of thiophene complexes of Mn,<sup>14a,b</sup> Ru,<sup>13,14c-e</sup> Rh,<sup>12,14f</sup> and Ir,<sup>12,14f</sup> however, no information is available on the bonding or the reactivity of thiophene on molecular molybdenum complexes.

The most commonly proposed structures for thiophene chemisorbed on a molybdenum-containing surface are schematically represented in Figure 1a. The corresponding molecular analogues formed by coordination of thiophene to molybdenum carbonyl fragments are shown in Figure 1b. It is also interesting to note at this point that molybdenum-carbonyl complexes have been used as starting materials for the synthesis of well dispersed, low valent molybdenum catalysts.<sup>38,39</sup>

(29) Pople, J. A.; Beveridge, D. L. *Approximate Molecular Orbital Theory*; McGraw-Hill: New York, 1970.

(30) Naray-Szabo, G.; Peterson, M. R. *J. Mol. Struct.* **1981**, *85*, 249.

(31) Friedman, P.; Allen, L. C. *Int. J. Quant. Chem.* **1986**, *29*, 1503.

(32) Arnesen, S. P.; Seip, H. M. *Acta Chem. Scand.* **1966**, *10*, 2711.

(33) Harshbrager, W. R.; Bauer, S. H. *Acta Crystallogr.* **1970**, *B26*, 1010.

(34) Muetterties, E. L.; Stein, J. *Chem. Rev.* **1979**, *79*, 479 and references therein.

(35) (a) Sung, S. S.; Hoffmann, R.; Thiel, P. A. *J. Phys. Chem.* **1986**, *90*, 1380. (b) Zonneville, M. C.; Silvestre, J.; Hoffmann, R. *J. Am. Chem. Soc.* **1986**, *108*, 1509.

(36) Crayston, J. A.; Almond, M. J.; Downs, A. J.; Poliakov, M.; Turner, J. *J. Inorg. Chem.* **1984**, *23*, 3051.

(37) Welch, J. A.; Peters, K. S.; Valda, V. *J. Phys. Chem.* **1982**, *86*, 1941.

(38) Sivasanker, S.; Yesodharan, E. P.; Sudhakan, C.; Brenner, A.; Murchison, C. B. *J. Catal.* **1984**, *87*, 514.

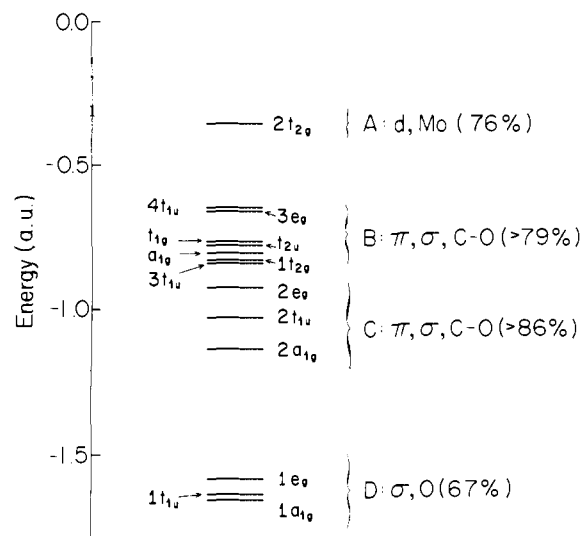


Figure 2. Classification of energy levels of  $\text{Mo}(\text{CO})_6$ .

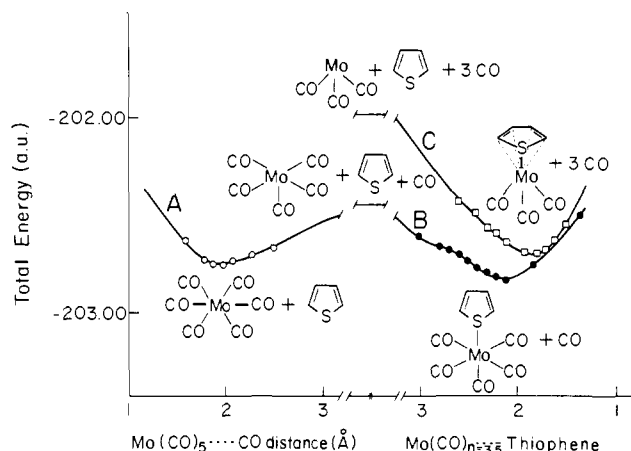
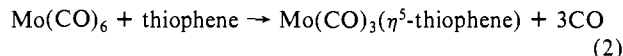
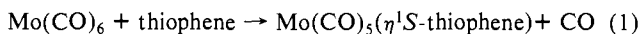


Figure 3. Potential energy curves for the formation of  $\text{Mo}(\text{CO})_6$  and  $\text{Mo}(\text{CO})_n$ -thiophene complexes ( $n = 3, 5$ ).

In the following sections we examine the formation of the two complexes shown in Figure 1b, by studying the reactions represented by eq 1 and 2. Before starting the analysis of the results



for the molybdenum-thiophene complexes, we will briefly discuss the CNDO results for the  $\text{Mo}(\text{CO})_6$  molecule in order to see how well they compare with more sophisticated theoretical methods and experimental data.

**2.  $\text{Mo}(\text{CO})_6$ .** A great deal of theoretical as well as experimental data concerning the interpretation of photoelectron spectra (PES) for this molecule has become available.<sup>40,41</sup> The classified energy levels of  $\text{Mo}(\text{CO})_6$  are depicted in Figure 2.

The order of the molecular energy levels is very similar to those of PES experimentally assigned,<sup>41</sup> except for the shifting in the  $e_g$  level to higher energies. The band A is associated to a  $2t_{2g}$  level and has a predominantly d character (76%). Band B is derived from  $\pi$  and  $\sigma$  CO orbitals with contributions greater than 79%, and it is the result of electrons on the  $4t_{1u}$ ,  $3e_g$ ,  $t_{1g}$ ,  $t_{2u}$ ,  $a_{1g}$ ,  $1t_{2g}$ , and  $3t_{1u}$  levels. Band C comes from CO (86%)  $\pi$  and  $\sigma$  orbitals ( $2e_g$ ,  $2t_{1u}$ ,  $2a_{1g}$ ). The D band is formed from  $\sigma$  orbitals ( $1e_g$ ,  $1a_{1g}$ ,

(39) Hucul, D. A.; Brenner, A. *J. Am. Chem. Soc.* **1981**, *103*, 217.

(40) Cooper, G.; Green, J. C.; Payne, M. P.; Dobson, B. R.; Hillier, I. H. *J. Am. Chem. Soc.* **1987**, *109*, 3836 and references therein.

(41) Higginson, B. R.; Lloyd, D. R.; Burroughs, P.; Gibson, D. M.; Orchard, A. F. *J. Chem. Soc., Faraday Trans. 2* **1973**, *69*, 1659.

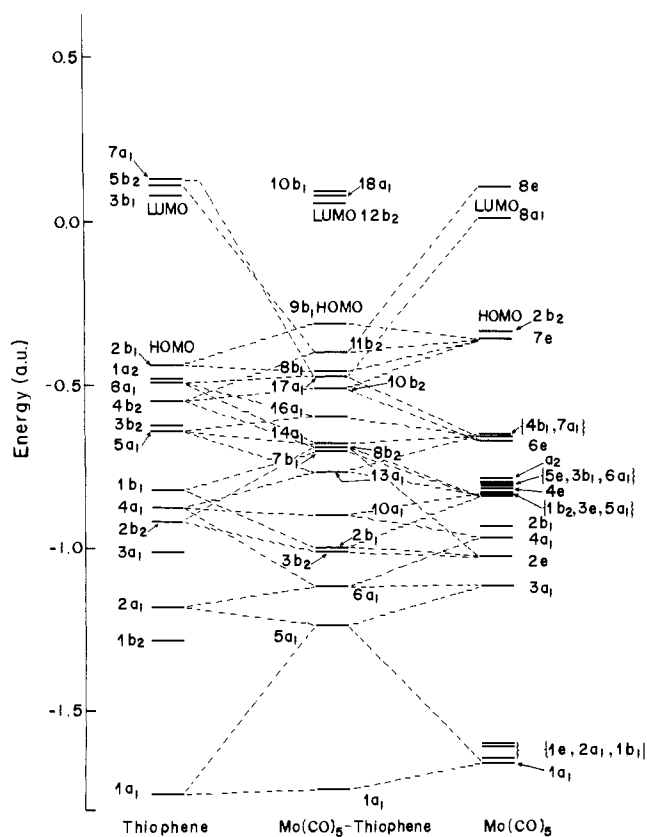


Figure 4. Correlation diagram of  $\text{Mo}(\text{CO})_5$ -thiophene.

$1t_{1u}$ ) with an oxygen contribution of 67%. All of these features of the nature of these levels concur very well with recent PES experimental results.<sup>40</sup>

A study of the dissociation of a Mo-CO bond from  $\text{Mo}(\text{CO})_6$  was carried out in order to determine the potential energy curve as shown in Figure 3. The value of the equilibrium bond length is about 2.00 Å which compares very well with the experimental value of 2.07 Å.<sup>33</sup> However, the Mo-CO binding energy is highly estimated.

Results of charge transfer in  $\text{Mo}(\text{CO})_6$  indicate that the Mo atom has an electronic net charge of 1.58  $e^-$ . This negative charge is probably too high although recent relativistic Dirac scattered wave calculations<sup>42</sup> give a molybdenum charge of 2.13  $e^-$ .

Thus, in general, the electronic properties of  $\text{Mo}(\text{CO})_6$  are qualitatively well-represented in these calculations, and, therefore, reasonable results for other Mo-CO complexes are expected.

**3.  $\text{Mo}(\text{CO})_5(\eta^1\text{S-thiophene})$ .** The formation of this complex is assumed to go via a  $\text{Mo}(\text{CO})_5$  intermediate which has been detected by IR spectroscopy of  $\text{Mo}(\text{CO})_6$  after UV photolysis.<sup>36</sup> In Figure 3, the potential energy curve A represents the formation of  $\text{Mo}(\text{CO})_5$  and the curve B the reaction of  $\text{Mo}(\text{CO})_5$  with thiophene to form  $\text{Mo}(\text{CO})_5(\eta^1\text{S-thiophene})$ , as it was proposed in eq 1. The results reveal that the approaching of thiophene to the uncoordinated site (vacancy) on the  $\text{Mo}(\text{CO})_5$  fragment is attractive which indicates that the products would be more stable than the reactants. This result intimates that even though the  $\eta^1\text{S}$ -complex has not been synthesized as yet, its existence is possible. With the purpose of understanding in more detail the formation of the thiophene- $\text{Mo}(\text{CO})_5$  complex, in Figure 4 we present the corresponding correlation diagram where only those energy levels of the complex that have a significant contribution from the S and Mo atomic orbitals are drawn. The nature of the molecular orbitals of the  $\eta^1\text{S}$ -complex are presented in Figure 5 where the interactions between the S and Mo atoms are depicted for each molecular orbital shown in Figure 4. The top atomic orbitals come from S and the bottom ones are from Mo.

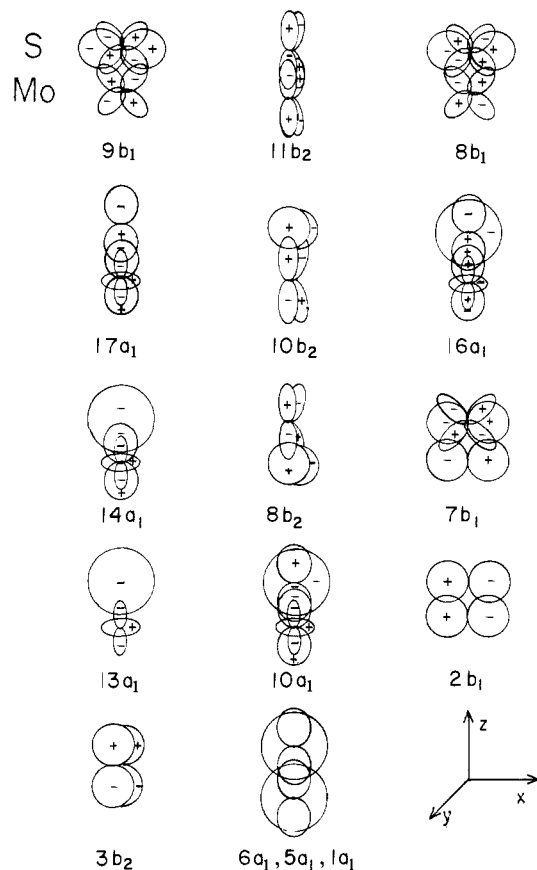


Figure 5. Orbital interaction between S-Mo for each molecular orbital shown in Figure 4.

The HOMO of the  $\text{Mo}(\text{CO})_5$  fragment has a  $b_2$  symmetry; however, this orbital does not interact because it is a  $d_{xy}$  orbital localized over the Mo atom. The active highest occupied molecular orbital (AHOMO) is of  $e$  symmetry, while the LUMO is of  $a_1$ . The AHOMO and LUMO coincide in symmetry with the HOMO and LUMO calculated by Ziegler et al.<sup>43</sup> with density functional theory. In the case of thiophene, the HOMO is  $2b_1$ . Nevertheless, another set of calculations<sup>44,45</sup> reports the  $a_2$  as HOMO. The  $a_2$ , in our calculations, is delocalized over thiophenic carbons with a very small contribution of  $S(d_{xy})$  orbital. The interaction of  $7e$  of  $\text{Mo}(\text{CO})_5$  and  $2b_1$  of thiophene, shown in Figure 4, produces the two molecular orbitals  $8b_1$  and  $9b_1$  (HOMO) which have bonding and antibonding character, respectively. Because the  $2b_1$  is more stable than  $7e$ , a partial transfer of charge from Mo to S is expected. A glance at Figure 5 shows that these orbitals are  $\pi$  ( $d-p$  and  $d-d$ ) type and reveals that a  $\pi$  donation will occur to the thiophenic ligand. The combination of  $6a_1$  of thiophene with  $7a_1$  of the  $\text{ML}_5$  fragment to form  $16a_1$  and  $14a_1$  (see Figure 4) produces a different situation. Here, an electronic transfer from S to Mo is expected because of the greater stability of the  $\text{Mo}(7a_1)$  orbital with respect to  $\text{S}(6a_1)$ . The interaction is  $\sigma(pz-pz, s-pz, s-dz^2, pz-dz^2)$  as schematically shown in Figure 5. The molecular orbitals  $17a_1$ ,  $13a_1$ , and  $10a_1$  are  $\sigma$ -type and result from an intricate and coupled interaction between thiophene ( $7a_1$ ,  $6a_1$ ,  $5a_1$ , and  $4a_1$ ) orbitals with  $\text{Mo}(\text{CO})_5$  ( $8a_1$ ,  $7a_1$ ,  $5a_1$ , and  $4a_1$ ) ones where the simple picture of bonding and antibonding orbitals is not clear at all. A similar complex interaction occurs in the orbitals  $11b_2$ ,  $10b_2$ ,  $8b_2$ ,  $7b_1$ ,  $2b_1$ , and  $3b_2$  which contribute to the formation of  $\pi$  bonds ( $d-d$ ,  $p-d$ , and  $p-p$ ) (see Figure 5). They are the result of the interaction of ( $5b_2$ ,  $4b_2$ ,  $2b_2$ , and  $1b_1$ ) thiophenic orbitals

(43) Ziegler, T.; Tschinke, V.; Ursenbach, C. *J. Am. Chem. Soc.* **1987**, *109*, 4825.

(44) Gelvis, U.; Roos, B.; Siegbahn, P. *Theor. Chim. Acta (Berlin)* **1972**, *109*, 4825.

(45) Von Niessen, W.; Kraemer, W. P.; Cederbaum, L. S. *J. Elect. Spect. Relat. Phenom.* **1976**, *8*, 179.

(42) Arratia-Perez, R.; Yang, C. Y. *J. Chem. Phys.* **1985**, *83*, 4005.

**Table II.** Atomic Orbital Populations of CO, Thiophene, Mo(CO)<sub>5</sub>, Mo(CO)<sub>5</sub>(η<sup>1</sup>S-thiophene), and Mo(CO)<sub>3</sub>(η<sup>5</sup>-thiophene)

		SC <sub>4</sub> H <sub>4</sub> or CO	Mo(CO) <sub>5</sub>	Mo(CO) <sub>5</sub> (η <sup>1</sup> -SC <sub>4</sub> H <sub>4</sub> )	Mo(CO) <sub>3</sub>	Mo(CO) <sub>3</sub> (η <sup>5</sup> -SC <sub>4</sub> H <sub>4</sub> )
S	s	1.776		1.338 (-0.438)		1.631 (-0.145)
	p	3.756		3.515 (-0.241)		3.359 (-0.396)
	d	0.532		1.086 (+0.554)		0.848 (+0.317)
	total	6.064		5.940 (-0.123)		5.838 (-0.224)
$\bar{C}$	s	1.036		1.026 (-0.010)		0.975 (-0.061)
	p	2.963		2.999 (+0.034)		2.924 (-0.039)
	total	3.999		4.024 (+0.024)		3.898 (-0.101)
$\bar{H}$ Mo	s	0.985		1.000 (+0.015)		0.973 (-0.012)
	s		0.411	0.438 (+0.027)	0.309	0.418 (+0.109)
	p		1.106	1.305 (+0.199)	0.710	1.279 (+0.569)
	d		5.762	5.670 (-0.092)	5.580	5.639 (+0.059)
	total		7.279	7.414 (+0.135)	6.599	7.337 (+0.738)
$\bar{CO}$	s	3.523	3.132	3.129 (-0.003)	3.117	3.103 (-0.014)
	p	6.477	6.612	6.581 (-0.031)	6.683	6.676 (-0.007)
	total	10.000	9.744	9.710 (-0.034)	9.800	9.779 (-0.021)

**Table III.** Bond Orders of Thiophene, Mo(CO)<sub>5</sub>, Mo(CO)<sub>3</sub>, Mo(CO)<sub>5</sub>(η<sup>1</sup>S-thiophene), and Mo(CO)<sub>3</sub>(η<sup>5</sup>-thiophene)

		SC <sub>4</sub> H <sub>4</sub>	Mo(CO) <sub>5</sub>	Mo(CO) <sub>5</sub> (η <sup>1</sup> -SC <sub>4</sub> H <sub>4</sub> )	Mo(CO) <sub>3</sub>	Mo(CO) <sub>3</sub> (η <sup>5</sup> -SC <sub>4</sub> H <sub>4</sub> )
Mo-S	sp-sp			1.24		0.92
	sp-d			0.61		0.40
	d-d			0.60		0.40
	total			2.45		1.72
Mo-C <sub>1</sub>	sp-sp			0.07		0.57
	sp-d			0.01		0.22
	total			0.08		0.79
Mo-C <sub>2</sub>	sp-sp			0.00		0.47
	sp-d			0.00		0.15
	total			0.00		0.62
Mo-CO	sp-sp		0.97	0.92	1.03	1.01
	sp-d		0.42	0.42	0.54	0.54
	total		1.39	1.34	1.57	1.55
C <sub>1</sub> -S	sp-sp	1.32		1.33		1.22
	sp-d	0.51		0.56		0.51
	total	1.83		1.89		1.73
C <sub>1</sub> -H	sp-sp	1.37		1.36		1.34
C <sub>1</sub> -C <sub>2</sub>	sp-sp	2.03		2.00		1.87
C <sub>2</sub> -C <sub>3</sub>	sp-sp	1.73		1.76		1.70

with (8e, 7e, 6e, 4e, and 2e) orbitals of the ML<sub>5</sub> fragment. Finally, in Figure 5, we also show the assistance of the most stable molecular orbitals (6a<sub>1</sub>, 5a<sub>1</sub>, and 1a<sub>1</sub>) which are associated with a σ(sp-sp) bonding.

In order to complement the information provided by the correlation diagrams, in Table II, we present the electronic population on the atomic orbitals of free CO, thiophene, Mo(CO)<sub>5</sub>, Mo(CO)<sub>5</sub>(η<sup>1</sup>S-thiophene), Mo(CO)<sub>3</sub>, and Mo(CO)<sub>3</sub>(η<sup>5</sup>-thiophene) molecules. The population changes of S, C, H, Mo, and CO, in the complexes, are in parentheses and are respectively referred to the population of Mo(CO)<sub>n</sub> (n = 3, 5) fragments and the thiophene molecule. The symbols  $\bar{C}$ ,  $\bar{H}$ , and  $\bar{CO}$  mean average population per atom. By comparing the population of different species in Table II, one can conclude the following.

(a) In the Mo(CO)<sub>5</sub> fragment, there is a transfer of charge from the CO ligands (0.256 e<sup>-</sup> per CO) to the molybdenum atom. The CO p-population (6.612 e<sup>-</sup>) increases with respect to the corresponding one in free CO (6.477 e<sup>-</sup>). An inverse situation takes place in the CO s-population which diminishes (-0.391 e<sup>-</sup>) with respect to the corresponding one in free CO. With the purpose of understanding in more detail this charge transfer, we separately calculate the CO σ and π calculations (6.000 and 4.000 e<sup>-</sup>, respectively) for free CO and Mo(CO)<sub>5</sub> (5.544 and 4.200 e<sup>-</sup>, respectively). In addition, the sums of the populations of the Mo atomic orbitals that form the σ and π bonds (1.765 and 5.541 e<sup>-</sup>, respectively) were evaluated. The above values for free CO and free Mo(d<sup>6</sup>s<sup>0</sup>p<sup>0</sup>) compared with the corresponding ones in Mo(CO)<sub>5</sub> indicate that the π(CO) population in Mo(CO)<sub>5</sub> increases while the π(Mo) decreases. The opposite situation is observed in the σ(CO) and σ(Mo) populations. These results are in agreement with the known synergic bonding mechanism by which the CO ligands donate electronic charge through the σ-bonds to the metal and the metal back-donates charge to the ligands

through the π bonds. It is good to note here that an internal reorganization of the s and p CO populations and the s, p, and d Mo populations can also take place besides the interatomic charge transfer.

(b) With respect to the Mo(η<sup>1</sup>S-thiophene)(CO)<sub>5</sub> complex, a net electronic transfer from CO to molybdenum is also observed (0.290 e<sup>-</sup> per CO) although it is larger than in the case of Mo(CO)<sub>5</sub>. Therefore, the total charge over Mo is greater (1.414 e<sup>-</sup>) in the complex than in the fragment (1.279 e<sup>-</sup>). The sulfur atom loses a small amount of electron density (-0.060 e<sup>-</sup>). However, the comparison with S in free thiophene (see values in parentheses) indicates that there is a redistribution of the orbital populations owing to the interaction with the metal. Although some charge is driven from the sulfur atom, the thiophene molecule receives a small amount of charge (0.036 e<sup>-</sup>). This charge is distributed through the ring in the p-orbitals of the thiophenic carbons and even in the hydrogen atoms (see in Table II, C and H values in parentheses).

In order to shed more light on the interpretation of the ML<sub>5</sub> fragment-thiophene interactions, in Table III, we present the (sp-sp, sp-d, and d-d) bond orders of the atoms of interest in thiophene, Mo(CO)<sub>5</sub>, Mo(CO)<sub>3</sub>, and the η<sup>1</sup>- and η<sup>5</sup>-complexes. The results show that in Mo(η<sup>1</sup>S-thiophene)(CO)<sub>5</sub> the most important S-Mo bonding is of sp-sp nature, and according to Figure 5 a variety of orbitals (17a<sub>1</sub>, 16a<sub>1</sub>, 14a<sub>1</sub>, 7b<sub>1</sub>, 10a<sub>1</sub>, 2b<sub>1</sub>, 3b<sub>2</sub>, 6a<sub>1</sub>, 5a<sub>1</sub>, 1a<sub>1</sub>) contribute to the formation of this bond. However, the d-orbitals of S and Mo take part in the bond. The d-d bonding interaction is represented by the top occupied orbitals (11b<sub>2</sub>, 8b<sub>1</sub>, and 9b<sub>1</sub>), and the sp-d bond is the resultant of many molecular orbitals, as shown in Figure 5.

The comparison of the bond orders (C-C, C-S, C-H, Mo-CO) for the η<sup>1</sup>S-complex, thiophene, and Mo(CO)<sub>5</sub> does not reveal any activation of these bonds. Nevertheless, we have to take into

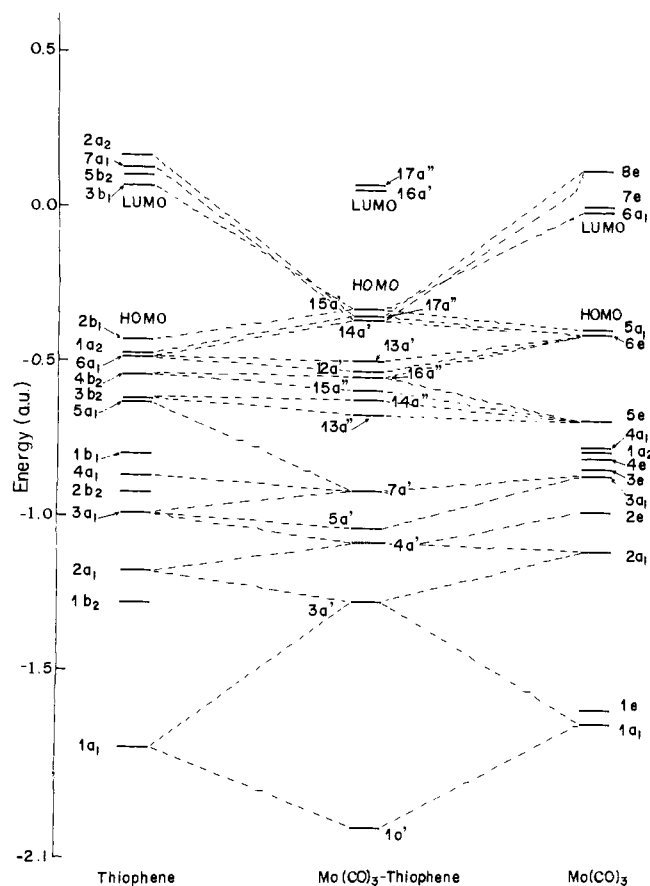


Figure 6. Correlation diagram of  $\text{Mo}(\text{CO})_3$ -thiophene.

account that the geometries of the interacting molecules have been maintained fixed in our calculations.

**4.  $\text{Mo}(\text{CO})_3(\eta^5\text{-thiophene})$ .** The favored geometry for this complex is that where the Mo atom is set in the direction perpendicular to the center of the line between the carbon atoms 1 and 4 shown in Figure 1b. The thiophenic plane is parallel to the plane formed by the carbonyls. Rotation of thiophene through the Z axis only changes the energy of the system by about 1 kcal/mol. The optimal Mo-S distance is 2.15 Å.

The potential energy curve shown in Figure 3 indicates that the formation of  $\text{Mo}(\text{CO})_3(\eta^5\text{-thiophene})$  from the  $\text{Mo}(\text{CO})_3$  fragment and thiophene is attractive. Nevertheless, the stability with respect to  $\text{Mo}(\text{CO})_5(\eta^1\text{S-thiophene})$  is lower. On the other hand, the products with respect to the reactants show a greater stabilization for the  $\eta^5$ -complex than in the case of the  $\eta^1\text{S}$ -complex. This result coincides with thiophene temperature programmed desorption (TPD) experiments on clean Mo surfaces<sup>6a,34</sup> because at low coverage the adsorbate which is parallel to the surface ( $\eta^5$ -complex) is more strongly attached to the surface than the perpendicular one ( $\eta^1\text{S}$ -complex).

The correlation diagram of the thiophene- $\text{Mo}(\text{CO})_3$  interaction is presented in Figure 6 in which only those molecular orbitals of the complex that have simultaneous contributions from Mo and thiophenic (S, C) atomic orbitals are considered.

The HOMO and LUMO orbitals for  $\text{Mo}(\text{CO})_3$  are  $5a_1$  and  $6a_1$ , respectively. Byers and Hall using the Fenske-Hall method<sup>46</sup> found that both HOMO and LUMO have an e symmetry. However, the difference in results can be explained by the fact that the e and  $a_1$  orbitals are in both calculations nearly degenerate, and it is possible that a switch between them can occur from one type of calculation to the other. Concerning the nature of these orbitals, the e is (57% d( $\delta$ ), 16% d( $\pi$ ), 27% CO) and the  $a_1$  is (75% d( $\pi$ ), 25% CO) which agrees with the results of Byers and Hall.<sup>46</sup> In Figure 7, the nature of the  $\text{Mo}(\text{CO})_3(\eta^5\text{-thiophene})$  energy levels

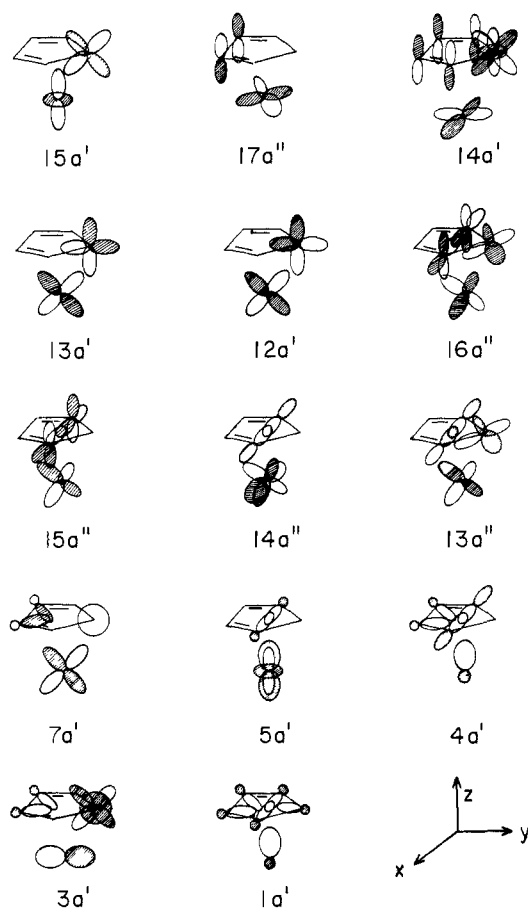


Figure 7. Orbital interaction between thiophene-Mo for each molecular orbital shown in Figure 6.

shown in Figure 6 are drawn by considering only the chief atomic orbitals of thiophene (C, S) and Mo. The HOMO ( $15a'$ ) aids to the formation of the Mo-S bond through a d-d interaction, as shown in Figure 7 and is mainly the result of the interaction of  $2b_1$  and  $3b_1$  thiophenic orbitals with the  $5a_1$  and  $6a_1$  of  $\text{Mo}(\text{CO})_3$  (see Figure 6). A careful look at Figure 6 shows that in our calculations the molecular orbital thiophene- $\text{Mo}(\text{CO})_3$  interactions do not result in a simple picture but are the product of multiple coupling between orbitals as in the case of the  $\eta^1$ -complex. Other orbitals that assist the formation of Mo-S bond are  $13a'$  and  $12a'$  which are the combination of  $6a_1$  of thiophene with  $6e$  of  $\text{Mo}(\text{CO})_3$  and are the result of a p-d interaction. The  $13a'$  respect to the  $12a'$  has some antibonding character because of the improper interaction of the  $\text{Mo}(d_{yz})$  orbital with the external lobe of the  $\text{S}(p_y)$ . There are other orbitals which also participate in the Mo-S bond with d-d ( $14a'$ ,  $16a''$ ,  $13a''$ ), d-s ( $7a'$ ) p-sd ( $3a'$ ), and sp-sp ( $1a'$ ) interactions as shown in Figure 7.

The formation of the bond between Mo and thiophenic carbons ( $C_1, C_4$ ) is to some extent the result of p-d coupling as in  $16a''$ ,  $15a''$ ,  $14a''$ , and  $13a''$  orbitals which are chiefly the product of  $4b_2$  and  $3b_2$  thiophenic orbitals with the  $6e$  and  $5e$  orbitals of  $\text{Mo}(\text{CO})_3$ . Some other participations in the building of the  $C_{(1,4)}\text{-S}$  bond come from p-d ( $14a'$ ), pd-sp ( $5a'$ ), and sp-sp ( $4a'$ ,  $1a'$ ) interactions. Finally, the bond between Mo and thiophenic carbons ( $C_2, C_3$ ) is a consequence of the interaction of p-d character ( $17a''$ ,  $7a'$ ). The  $17a''$  orbital is the resultant of the combination of  $2a_2$  and  $1a_2$  of thiophene with  $8e$  and  $6e$  of  $\text{Mo}(\text{CO})_3$ . In addition, some contributions from sp-sp couplings like  $1a'$ ,  $3a'$ , and  $4a'$  have to be considered because the carbon atomic orbitals have an  $sp^2$  hybridization which in general favors these Mo-C bonds.

The study of the transfer of charge can be easily visualized by analyzing the orbital population changes (see Table II) of Mo, S, C, and H as was done in the last section. The molybdenum atom has a negative charge of  $1.337 e^-$  which is the product of electronic drift from CO ligands ( $-0.663 e^-$ ) and a withdrawal

(46) Byers, B. P.; Hall, M. B. *Organometallics* 1987, 6, 2319.

from sulfur ( $0.162 e^-$ ), carbons ( $0.408 e^-$ ), and even from hydrogens ( $0.104 e^-$ ). By comparing the populations of the complex with the respective ones in thiophene and  $\text{Mo}(\text{CO})_3$  (see values in parentheses in Table III), we can obtain information on the effects of the interaction thiophene- $\text{Mo}(\text{CO})_3$  (horizontal chemisorption of thiophene on a one-center site). The CO ligands transfer less charge to the metal. The transfer to the Mo atom is mainly to the sp orbitals. The electronic sulfur drift is from the sp orbitals having also an increase of the d population. These results insinuate that the transfer from thiophene is mainly through the sp-sp interactions, as shown in Figure 7, although, another more complex mechanism cannot be discarded.

The transfer of charge from thiophene to the metal may be interpreted as an indication of the weakening of thiophenic bonds. In fact, recent experimental studies of thiophene adsorption on crystal surfaces of  $\text{Mo}^{6,8,47}$  and on a  $\text{MoO}_3/\gamma\text{-Al}_2\text{O}_3$  catalyst<sup>48</sup> reveal that the chemisorption at low coverage (parallel adsorption) is irreversible, and a decomposition of thiophene is observed. In general, at low coverage, the heat of adsorption is the highest owing to the fact that the adsorption sites are the most unsaturated ( $\text{Mo}(\text{CO})_3$ ). As the coverage increases close to saturation, only those sites that have a vacancy with one unsaturation are available ( $\text{Mo}(\text{CO})_5$ ), and the heat of adsorption is smaller due to a weaker bond adsorbate-substrate and a repulsive interaction adsorbate-adsorbate. A very important fact in relation to the reactivity of chemisorbed thiophene during HDS concerns the nature of the  $16a'$  (LUMO) orbital of  $\text{Mo}(\eta^5\text{-thiophene})(\text{CO})_3$  which is 73% located on the thiophenic ring, mainly on C-S bonds, and has an antibonding character. This suggests that nucleophilic attack to  $C_1$  or  $C_4$  can result in C-S bond scission, as occurs in nucleophilic reactions of the complex  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\eta^5\text{-thiophene})]^+ 14^d$  and of thiophenic molecules in general.<sup>49</sup> This supports the view that hydrogenolysis of C-S bonds is probably the step following chemisorption during HDS of thiophene. In the case of Mo-

$(\text{CO})_5(\eta^1\text{-thiophene})$ , the HOMO ( $9b_1$ ) is 70% on the Mo-S bond and the LUMO ( $12b_2$ ) is an orbital located on CO bonds, hence the activation of thiophenic bonds toward nucleophilic attack is not expected.

The analysis of the bond orders in Table III indicates that the bond between thiophene and Mo in  $\text{Mo}(\eta^5\text{-thiophene})(\text{CO})_3$  is chiefly sp-sp with some contributions of sp-d (Mo-C<sub>1</sub>, Mo-C<sub>2</sub>, and Mo-S bonds) and d-d (Mo-S bond). Again, the sulfur d-orbitals take part in the bonds through sp-d and d-d bonding interactions, see Figure 7.

It is also observed that the Mo-CO bond orders do not change by interaction of  $\text{Mo}(\text{CO})_3$  with thiophene. The C<sub>1</sub>-S, C<sub>1</sub>-C<sub>2</sub>, and C<sub>2</sub>-C<sub>3</sub> bonds have greater changes than in the  $\eta^1$ -complex, but as we noted in the previous section, geometrical relaxation would be necessary to observe a noticeable variation in the bond orders.

### Conclusions

(a) Our results suggest that although the complexes  $\text{Mo}(\eta^1\text{-S-thiophene})(\text{CO})_5$  and  $\text{Mo}(\eta^5\text{-thiophene})(\text{CO})_3$  have not been synthesized as yet, their formation is possible.

(b) The nature of the thiophene-metal bond is mainly sp-sp with some d-d and sp-d contributions. The d-sulfur orbitals participate in the metal-thiophene bond.

(c) There is a small transfer of charge from the metal to thiophene in the  $\eta^1\text{S}$ -complex and a noticeable drift of charge from thiophene to molybdenum in the case of the  $\eta^5$ -complex.

(d) The binding energy of thiophene in the  $\text{Mo}(\eta^5\text{-thiophene})(\text{CO})_3$  is greater than in  $\text{Mo}(\eta^1\text{S-thiophene})(\text{CO})_5$ , which correlates well with surface chemistry results.

(e) Activation of the C-S bonds of thiophene toward nucleophilic attack at  $C_1$  or  $C_4$  is expected in the case of  $\text{Mo}(\eta^5\text{-thiophene})(\text{CO})_3$ , whereas no such activation is apparent for  $\text{Mo}(\eta^1\text{S-thiophene})(\text{CO})_5$ .

**Acknowledgment.** This research could not have been accomplished without CONICIT's grants, S1-1846 and S1-1814, and the computational facilities of IVIC and IBM Scientific Center.

**Registry No.**  $\text{Mo}(\text{CO})_5(\eta^1\text{-thiophene})$ , 117095-45-1;  $\text{Mo}(\text{CO})_3(\eta^5\text{-thiophene})$ , 117095-46-2.

(47) Gellman, A. J.; Farias, M. J.; Salmeron, M.; Somorjai, G. A. *Surf. Sci.* **1984**, *136*, 217.

(48) Vattis, D.; Matralis, H.; Lycorghiotis, A. *J. Chem. Soc., Faraday Trans. 1* **1987**, *83*, 1179.

(49) Meth-Cohn, O. In *Comprehensive Organic Chemistry*; Sammes, P. G., Ed.; Pergamon Press: Oxford, **1979**; p 804.

## Surface Dynamics of Adsorbed Species on Heterogeneous Oxidation Catalysts: Evidence from the Oxidation of C<sub>4</sub> and C<sub>5</sub> Alkanes on Vanadyl Pyrophosphate

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**Abstract:** Steady-state and transient reactivity measurements, Fourier-transform infrared studies, and stopped-flow desorption analyses of the selective oxidation of C<sub>4</sub> and C<sub>5</sub> alkanes at the vanadyl pyrophosphate surface suggest that the surface dynamics of adsorbed species plays an important role in determining the selective oxidation pathways and the nature of the products of selective oxidation. The results indicate the possibility of two different oxidation pathways in maleic anhydride synthesis from *n*-butane which involve the intermediate formation of either a lactone or furan and which are characterized by different rates and selectivities. The presence of side methyl groups in the formation of similar intermediates from *n*-pentane decreases their reactivity and favors a parallel surface reaction between intermediates with the final formation of phthalic anhydride from the C<sub>5</sub> hydrocarbon. However, when the rate of conversion of the intermediates is increased, thus modifying the surface availability of oxygen, maleic anhydride also becomes the principal product from the C<sub>5</sub> alkane.

Recent developments of in situ characterization of adsorbed species during catalytic heterogeneous processes highlight their role in the self-organization of active surfaces (coadsorption enhancement effects, cocatalysis by strongly adsorbed substances,

...) as well as the influence of their surface mobility. For example, recent studies have shown<sup>1d</sup> the high rate of surface diffusion on

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(1) (a) Zaera, F.; Gellman, A. J.; Somorjai, G. A. *Acc. Chem. Res.* **1986**, *19*, 24. (b) Pimental, G. *Chem. Technol.* **1986**, *9*, 536. (c) Davis, S. M.; Zaera, F.; Somorjai, G. A., *J. Catal.* **1982**, *77*, 439. (d) Cevallos-Candau, J. F.; Conner, W. C. *J. Catal.* **1987**, *106*, 376.