JOURNAL OF CATALYSIS **111**, 409–417 (1988)

A Theoretical Study of PdCONa and $[PdCONa]^+$ Complexes as a Simple Model of a Promoted Catalyst

V. BONAČIĆ-KOUTECKÝ,* J. KOUTECKÝ,* P. FANTUCCI,† AND V. PONEC‡

**Institut of Physical and Theoretical Chemistry, Free University Berlin, Takustrasse 3, 1000 Berlin 33, Federal Republic of Germany; †Department of Inorganic and Metallorganic Chemistry, CNR Center, University of Milan, Via Venezian 21, 20133 Milan, Italy; and ‡Gorlaeus Laboratory, State University of Leiden, P. O. Box 9502, 2300 RA Leiden, The Netherlands*

Received February 23, 1987; revised June 12, 1987

The electronic structure of the PdCO complex interacting with a neutral or ionic Na center has been studied by means of SCF-CI calculations. The neutral PdCONa complex is found to be only slightly more stable (about 25 kJ mol^{-1}) than the PdCO + Na system when the sodium atom directly interacts with the carbonyl group, while repulsion occurs when the sodium atom interacts with the Pd atom as in Na–Pd–CO. An energetically much more favorable situation is found for the case in which the PdCO complex is perturbed by a Na^+ ion. The $[PdCONa]^+$ complex shows an extra stabilization of 63–92 kJ mol^{-1}, accompanied by an increase in the C–O and a decrease in the Pd–C distances, with respect to the unaffected PdCO complex. The main effect of the Na^+ ion seems to be of an electrostatic nature, bringing the CO molecule toward an enhanced donor and acceptor capability. Similarities between the electronic structure and the minimum geometries computed for the $[PdCONa]^+$ complex and those characteristic of a CO molecule adsorbed on an alkali-promoted catalyst are suggested. © 1988 Academic Press, Inc.

INTRODUCTION

Although the systems studied in this paper are of some interest per se, the main motivation for the study is a potential relation with the phenomenon of catalytic promotion. Promoters can be described as substances which themselves are of zero or negligible catalytic activity, but which, when added to an active catalyst, improve the catalyst activity, selectivity, and/or stability. Promoters have been used from the early days of catalytic practice. For example, the first industrial ammonia synthesis catalyst consisted of iron, Al_2O_3, and K_2O, and its composition was optimized by about 20,000 experiments (*1*). The high number of experiments needed was due to the "trial and error" approach, the only possibility left when no ideas about the function of promoters are available.

Catalytic practice still makes extensive use of promoters (*2, 3*), but very little is yet known definitively about their exact function and even nowadays many catalysts are still being designed empirically. However, there are already some ideas available in the literature which can form a basis for a discussion about the action of promoters. For example, in relation to catalysis by metals and promotion by alkalis, the following ideas have been suggested:

1. The promoter acts "through the metal" and its influence can be thus of a "long-range" character. This is a very widely accepted view and as far as alkalis are concerned, it is usually assumed that they stimulate the donation of electrons out of the metal (see, for example, Ref. (*4*)).
2. The promoter forms "localized" chemical bonds with the reacting molecules or reactive intermediates of the reaction; interaction is thus of a "short-range" character. The bond strengths expected by various authors vary widely (see, e.g., Ref. (*5*)).
3. The electrostatic field in the nearest neighborhood of a promoting species influences the binding with the metal and/or the

0021-9517/88 $3.00

reactivity of adsorbed molecules. This is a "medium-range" interaction, a "through the vacuum" effect (Ref. (*6*)).

Points 1–3 do not represent a full inventory of the proven or possible effects of alkalis. For example, the effects of alkalis on the "ensemble size" achieved by blocking of the surface atoms, the effects on the bifunctionality (acidic function) of the catalysts, the effects of the presence of a promoter on the morphology of the metal, etc., are not listed under 1–3 and are also not discussed any further. However, the points cited above are the main ideas which can be related to the subject of this study. A full account of surface science studies on promoters is given in a recent study by Uram *et al.* (*7*).

A few words about the approach of this paper are needed at this stage. A full system (a metal, promoter, and reacting molecule(s)) is too complicated to be analyzed by quantum chemical methods of any accuracy. In this paper only the simplest possible model system has been computed but the theoretical method used can in principle supply rather accurate information, as has been shown by previous papers (*8*).

Consequently, only several representative geometrical arrangements have been investigated, chosen so that either Na or Na^+ interacts with Pd and directly with CO, representing promotion "through the metal" and "through space," respectively.

METHOD

Computational Procedure

The energetics accompanying the interaction between the PdCO complex with a neutral Na atom or with a Na^+ cation have been investigated employing the Hartree–Fock (HF) and configuration interaction (CI) method. In order to reduce the computational effort, the core electrons of the Pd and Na atoms have been replaced by an effective core potential (ECP) (*9*). The parameters entering the definitions of the ECP operators have been taken from Refs. (*10*, *11*), for Pd and Na, respectively. The adopted Gaussian basis set is of type (5, 2, 6/3, 1, 3) for Pd (8b) and (4, 3/2, 1) for Na (*11*), respectively. Huzinaga's basis (7, 3/4, 2) for C and O atoms has been augmented by a single *d* polarization function with exponents equal to 0.6 and 1.154, respectively (*12*). All the *d* shells are treated as consisting of six Cartesian Gaussian functions.

The molecular wavefunction computed according the HF method can be substantially improved by means of a CI treatment. In the present study the MRD-CI method (*13*) has been adopted, accepting however some simplifications because the potential hypersurfaces have several dimensions and, consequently, the number of energy evaluations can be quite high. Therefore, in order to reduce the computational cost, the CI treatment has been limited only to those configurations which are singly and doubly excited with respect to the HF configuration only (SD-CI). The selection–extrapolation technique of the MRD-CI method (*13*) is applied with an energy threshold of 2.5 microhartree (1 hartree = 2626 kJ mol^{-1}). The dimension of the secular determinant can be as large as 8500, the case of the most complex system considered (PdCONa), in C_s symmetry.

A possible source of error in the molecular energy evaluation when ECP methods are used is the assumption that the two-center core–core repulsion can be simply evaluated using the point-charge approximation for the effective core charges. In order to test the validity of such an approximation, with the PdCONa complex (in which atoms with large cores are present) also the true core–core potential has been evaluated for all ion pairs occurring in the complex. In this test case a minimum basis set (15, 9, 6/5, 3, 1) and (9, 3/3, 1) has been used to describe the core electrons of Pd and Na atoms, respectively. It has been found that only in the case of large core ions (Pd^{10+} and Na^+) does the true core–core potential slightly deviate from the simple point-charge values. The deviations never exceed 2.1–4.2 kJ mol^{-1}, in all ranges of distances relevant for chemical bonding. Since such corrections are certainly small in comparison with the overall accuracy of the present computational scheme, they have been neglected.

RESULTS AND DISCUSSION

The computational method described above has been applied to the study of the changes in stability and geometry of the PdCO complex when it is approached by a neutral or positively charged sodium atom.

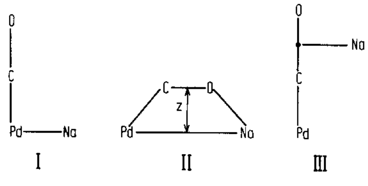
The first set of calculations has been carried out on the free CO molecule and PdCO complex. The results have shown that a fairly good basis set and a CI treatment are needed in order to obtain meaningful geometry–energy relationships.

The simplest approach to the description of the electronic structure of the PdCO complex is the ECP-HF method, applied without considering polarization functions on C and O atoms. This treatment gave for the equilibrium bond distances Pd–C and C–O the values 4.36 and 2.136 atomic units (a.u.) [1 a.u. = 0.5297 Å], respectively, but the resulting complex does not appear to be stable with respect to the fragments in their ground state. Moreover, the equilibrium distance of the free CO found at the ECP-HF level (2.133 a.u.) agrees with the experimental value (2.132 a.u. (*14*)) but the agreement is worse (the distance becomes longer) when the energies are reoptimized at the CI level (2.19 a.u.).

Using the atomic basis set mentioned above, but now including the *d* polarization functions on C and O, the CI treatment of the free CO molecule (14 electrons) gave an equilibrium distance of 2.134 a.u. and a harmonic frequency of 2152 cm^{-1}. Both values are in good agreement with the experimental ones (*14*), showing that this description of the CO molecule is fairly accurate.

The electron correlation effects are also very important as far as the stability of the PdCO complex is concerned. At the CI level (20 electrons) the stability of PdCO is computed to be 30.1 kJ mol^{-1}, the Pd–C distance (4.05 a.u.) is found to be 0.32 a.u. shorter than the HF value, while the length of the C–O bond is computed as being identical to that of the free CO molecule. The present results on the PdCO complex confirm essentially our previous findings (*8*). However, they still cannot be considered as accurate in the absolute sense, since the SD-CI treatment adopted here is always affected by a size consistency error. However, in the present context, this does not represent a serious drawback, since the energy and geometry of the free PdCO complex are used as reference data with respect to which the energy–geometry perturbation produced by the approaching Na or Na^+ will be evaluated. This is certainly true considering that the correlation energy for PdCO + Na (a one-electron atom) or Na^+, at infinite distance, is equal to that of the free PdCO.

A few remarks justifying the models used are now appropriate. The models [I–III] are shown in Scheme 1, and they all have some relation to the catalytic problems. As already mentioned above, some authors (*4*) assume that the promoters influence the reaction components adsorbed on the metal, through the metal; by the way, they also influence at longer distances. Such an influence should be the strongest in configurations which can be represented by the model under "I" of Scheme 1. Strong local interactions can be expected to lead to the formation of such configurations as in "II" or "III" of Scheme 1. Model II is seen as having a relation to the "tilted-CO" com-



SCHEME 1. Configuration of the [Pd + CO + Na] complexes considered in the calculations.

plexes while III represents the "CO-side-on" complexes (*4, 5, 15–17*).

The neutral system Pd + CO + Na has been investigated in detail in the geometry configurations I and II shown in Scheme 1. In structure I the Na atom directly interacts with the palladium atom. In this case, no attempts have been made to vary the Pd–Na distance. This distance has been kept constant at the value of 5.14 a.u., which is the equilibrium distance computed for the PdNa diatomic species. When the Pd–C distance varies in the range 3.8–4.6 a.u., while the C–O distance is fixed at the value of 2.134 a.u. the interaction energy curve always shows a repulsive behavior, with only a small inflection on the curve at Pd–CO = 4.25 a.u. The stretching of the C–O bond further increases the repulsive character of the potential, showing that this configuration (I) does not correspond to any energetically favorable perturbation of the PdCO complex by Na. Since the repulsive nature of the curve is pronounced (~50 kJ mol^{-1} for C–O = 2.134 a.u. and Pd–C = 4.05 a.u.), it is to be expected that the variation of the Pd–Na distance will not substantially influence the overall behavior. The curve is also repulsive for the cationic system with structure I as will be discussed later.

A more favorable situation is found in the case of configuration II of Scheme 1. In this configuration the neutral Na atom can directly perturb the CO molecule, but does not significantly perturb the Pd atom due to the large distance (Pd–Na > 10 a.u.). A shallow minimum is found for the collinear structure ($z = 0$, see Scheme 1) showing a stabilization of about 25.1 kJ mol^{-1} and Pd–C and C–O distances of 3.78 and 2.16 a.u., respectively. It is worth noting that a significant contraction of the Pd–C bond and an elongation of the C–O bond is accompanied by a relatively small increase in the total stability of the complex. However, considering that in order to bring the free PdCO complex into the same distorted geometry an energy expense of about 21 kJ mol^{-1} is needed, it is apparent that the variations of the Pd–CO and PdC–O bonds can be easily understood in terms of the commonly accepted views of coordination chemistry as being due to an increased π back bonding from the metal to the coordinated carbon monoxide.

For configuration III of Scheme 1, distances Pd–CO = 3.7 a.u. and PdC–O = 2.13 and 2.17 a.u. have been considered, while the length of the "*–Na" bond (where the asterisk signifies the midpoint of the C–O bond; see Scheme 1) is allowed to vary in the range 3.5–8.5 a.u.

For both the short and long C–O distances, the interaction is found to be always repulsive, but this character is much less pronounced in the case of the shorter C–O bond length.

With the $[PdCONa]^+$ complex, several calculations performed for configuration I of Scheme 1 have shown that this configuration is energetically unfavorable, similar to the case of the corresponding neutral complex.

More extensive investigation has been carried out for the molecular arrangements II and III of Scheme 1. In both cases a nearly full study of the hypersurface has been made with the only constraints that the four atoms lie always in the same plane and that in configuration III the sodium atom points always at the midpoint of the C–O bond.

For configuration II the following ranges of the internuclear distances have been considered: Pd–CO 3.5–4.05 a.u., PdC–O 2.13–2.33 a.u., and PdCO–Na 3.8–6.5 a.u. and z 0–2 a.u. (z is the deviation from the CO linearity; see Scheme 1). A well-defined minimum was found for all z values used. In particular, for $z = 0.63$ a.u., Pd–C = 3.87 a.u., and C–O = 2.19 a.u. an absolute minimum is found, which corresponds to a stabilization energy of 93.6 kJ mol^{-1}. The Pd–Na distance at the minimum energy is equal to 10.5 a.u. The dependence of the PdCO–Na^+ interaction energy upon the four considered internal coordinates is displayed in

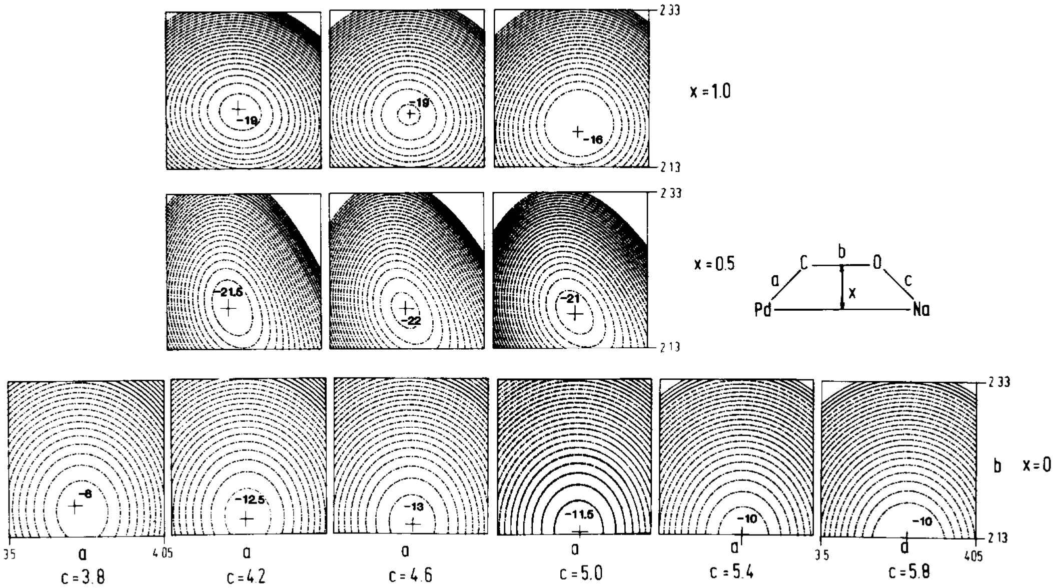


FIG. 1. Energy surfaces for the $(Pd\text{–}CONa)^+$ complex. The stabilities (kcal mol^{-1}) are computed with respect to $E(Pd\text{–}CO) + E(Na^+)$. The isoenergetic contours are plotted with $\Delta E = 0.5$ kcal mol^{-1} = 2.09 kJ mol^{-1}. The local minima are indicated by + and the corresponding energy values are given in kilocalories per mole.

Fig. 1 in the form of equipotential energy curves. It is apparent that in the region around the minimum the curvature of the surface along the Pd–C coordinate is higher than that in the regions characterized by long O–Na distance. Moreover, the C–O distance values corresponding to local minima at constant values of the z coordinate progressively increase as z increases. Correspondingly, the curvature along the C–O coordinate progressively decreases.

In the case of configuration III, the following distances in $[PdCONa]^+$ complex have been considered: Pd–C 3.7–4.05 a.u., C–O 2.13–2.33 a.u., and $*$–Na 4.5–6.5 a.u., respectively. The minimum located at Pd–C = 3.76 a.u., C–O = 2.16 a.u., and $*$–Na = 5.61 a.u. corresponds to a stability of 63 kJ mol^{-1}.

In addition, the angle of Pd–C–O in arrangement III has been varied in the interval [160–220°], simulating tilted structures, but no further energy stabilization has been achieved. In contrast, the energy increases with respect to the minimum for the midpoint structure III in the range from 35 to 23 kJ mol^{-1}. This is the reason why the models in which Na^+ is not constrained to the midpoint of the C–O bond have not been investigated in more detail.

In order to interpret, at least at a qualitative level, the nature of stabilization which characterizes the $[PdCONa]^+$ complex, the Mulliken population analysis will be discussed for three different geometries of such a complex, namely, configuration II in the collinear form ($z = 0$ a.u., case A) and in trapezoidal form ($z = 0.63$ a.u., case B) and finally configuration III in its equilibrium geometry (case C). These three cases are compared with the data of the free PdCO complex (case D) in Table 1.

It has been found that in case B, due to the relatively small displacement from linearity, the π degeneracy is still present almost completely. In particular, the energy splitting of the two MOs with the largest similarity with the 1π MO of the free CO molecule does not exceed 0.3 eV. Correspondingly, the two "π" components have

TABLE 1

Charge Distribution in PdCO and $PdCONa^+$ Complexes[a]

	PdCO	$PdCONa^+$		
		(II, z = 0 a.u.)[b]	(II, z = 0.63 a.u.)[c]	(III)[d]
σ_C	4.6131	4.5838	4.5726	4.5859
π_C	1.1726	1.1207	1.1193	1.2291
σ_O	5.2378	5.2141	5.2217	5.2125
π_O	2.9263	3.0871	3.0999	2.9393
σ_{CO}	9.8509	9.7979	9.7943	9.7983
π_{CO}	4.0989	4.2078	4.2192	4.1684
Q_{CO}	0.0502	−0.0065	−0.0149	0.0290
σ_{Pd}	2.1491	2.1718	2.1528	2.1982
π_{Pd}	3.9011	3.7795	3.7970	3.8172
δ_{Pd}	3.9997	3.9992	3.9905	3.9967
Q_{Pd}	−0.0500	0.0495	0.0597	−0.0121
Q_{Na}	—	0.9569	0.9556	0.9798

[a] All the populations are quoted in terms of the $C_{\infty v}$ nomenclature. For the sake of simplicity the populations of the δ orbitals of C and O atoms are not reported.

[b] With equilibrium geometry for collinear form II of Scheme 1.

[c] With equilibrium geometry (z = 0.63 a.u.) of form II.

[d] With equilibrium geometry of form III.

very similar p_π atomic orbital occupancy: 0.5615, 0.5592 for C and 1.5512, 1.5487 for O. The effect caused by the displacement from linearity is negligible for *M*Os with large components from the π or δ orbitals of the Pd atom. Despite the fact that in case C the distortion from linearity is much more pronounced, our results show that both the energy splitting of the "π" components (0.4 eV) and the difference in the electron occupancy of the p_π orbitals (0.6071, 0.6220 for C and 1.4788, 1.4605 for O) are quite small. The results therefore justify the fact that in Table 1 the Mulliken analysis data of all investigated complexes are reported in terms of the $C_{\infty v}$ nomenclature.

The positive charge of $[PdCONa]^+$ complexes is always strongly localized on the Na center (see Table 1). The Na^+ actually seems to induce mainly an electrostatic effect (see Table 1).

When the electron distribution of the unperturbed PdCO complex is compared with that of the cationic $[PdCONa]^+$ species, it is apparent that the electron charge transferred by the "π mechanism" from the metal to the CO moiety increases and does so in the order D(0.10) < C(0.17) < A(0.20) < B(0.21). Also the amount of σ charge donated formally from CO to the metal atom increases in the same order: D(0.15) < C(0.20) ≃ A(0.20) < B(0.21). This means that in the presence of the Na^+ ion both the σ and the π contributions to the Pd–CO bond are enhanced. The stability of the complexes nicely parallels the extent of the π back bonding and σ bonding effect which are responsible for a strengthening of the Pd–C and a weakening of the C–O bond, in agreement with the usual views of coordination chemistry. The overall effect is further illustrated by the variations in the computed bond distances.

As far as the effect is concerned, caused by the presence of the Na^+ ion on the core and valence *M*O levels of the CO molecule, it must be noted that in the $[PdCONa]^+$ species these levels are stabilized (in comparison with the unperturbed PdCO compound) by a nearly constant energy of about 4–5 eV. Moreover, the energy stabilization seems to be quite independent of the particular geometry of the complex and never produces a change in the *MO* energy sequence as illustrated in Fig. 2. This further confirms the conclusion that the main effect of the Na^+ ion is of an electrostatic nature.

Let us now turn our attention to the implications which our study might have for chemisorption and catalysis.

The information obtained by temperature-programmed desorption/thermal desorption spectroscopy (TPD/TDS) shows that the presence of alkali metals next to CO considerably increases the temperature at which CO desorbs. The expected order of the increase in the CO heat of adsorption agrees well with the stabilization which we found for $[Pd + CO + Na]^+$ complexes in configurations II and III (Scheme 1). Actually, configuration III with a stabilization of 63 kJ mol^{-1} seems to be nearer to the experimental data (*7*). Such stabilization is not achieved with Na^0 but this is not surprising since on metals Na is very strongly polarized in the sense of Na^+ formation.

In the literature (*5, 7, 15–17, 18*) discussion is still going on as to whether in the presence of an alkali metal (or ion) the orientation of CO is "tilted towards the alkali ion" or "perpendicular, side-on adsorbed to the promoter." Photoemission and Auger spectra seem to provide support for the "side-on" configuration. This is certainly not in contradiction with our calculations which reveal that the "side-on" configuration leads to a sufficient stabilization to comply with the TPD/TDS data.

It appears (see Table 1) that no substantial "rehybridization" (redistribution of electrons) occurs on CO. This means that the IR spectra of CO on promoted surfaces, and the EELS (electron energy loss spectroscopy) data, must be explained by the Stark effect, as already suggested by others (*7, 19–22*). There is an electrostatic effect on the energy levels of PdCO (see Fig. 2) but it causes rather limited changes in the occupation of individual levels (Table 1) and it is not expected (see (*19*)) that this alone would lead to such large effects on the IR and EELS spectra as observed (see, e.g., Ref. (*7*)).

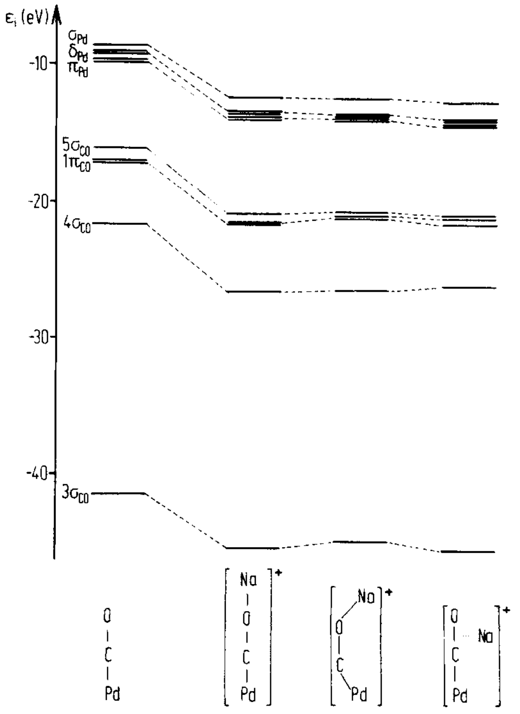


FIG. 2. Valence *MO* energies for the complexes indicated at the bottom.

It should be mentioned that our conclusions with regard to the redistribution of electrons (in CO, by Na^+), which has been called rehybridization (*18*), are at variance with the interpretation which various authors give to their data (*15, 18*). The exact reason for this discrepancy requires further study. However, it is worthwhile noting that in a recent theoretical paper Wimmer *et al.* (*23*), using theoretical techniques different of ours, come to the same conclusions as we do above. However, Wimmer *et al.* (*23*) use a method which models the metal as a thin slab of atoms, which can show many of the metallic properties. Thus, the mere limitation of our calculations to single-metal-atom complexes is not the reason for the difference between our conclusions and those of the authors of

Refs. (*15, 18*). Moreover, the theoretical approach using the "jellium" model leads to conclusions similar to ours (*6, 7*).

There is one more point concerning catalysis and chemisorption. We have mentioned already that some authors (e.g., see Ref. (*4*)) prefer to speculate on the action of promoting atoms or ions as being "through the metal," instead of "through the vacuum." If such an effect were real it should be visible as stabilization in structure I (Scheme 1). However, no appreciable stabilization occurs in this configuration. Recent experimental work (*21, 24*) has brought also some empirical evidence against the "through the metal" effects: a promoter *on* the Rh surface influences the activity and selectivity in syngas (CO/H_2) reactions but this effect is absent when the same promoting component is only *under* Rh particles as a support (*24, 25*).

CONCLUSIONS

The following conclusions can be derived from the data presented and the discussion.

(i) A Pd–CO complex is better stabilized by sodium in its ionic than in its neutral form; Na^+ increases the stability by 29–93 kJ mol^{-1}.

(ii) Na^+ induces a decrease in the Pd–C bond length and an increase in the CO (3%) bond length.

(iii) Na^+ enhances the σ and π mechanisms of Pd–CO bonding.

(iv) The main effect of Na^+ is like that of a point charge, essentially an electrostatic effect. The effect can occur in various configurations, in qualitative agreement with the experimental data (*7*).

(v) The calculations and their results do not support the idea of a "through the metal" effect; the effect is rather "through the vacuum." The last two points (iv and V) have implications in the theory of catalytic promoting effects.

REFERENCES

1. Mittasch, A., "Advances in Catalysis" (Frankenburg, W. G., Komarewsky, V. I., and Rideal, E. K., Eds.), Vol. 2, p. 82. Academic Press, San Diego, 1950.

2. Innes, W. B., *in* "Catalysis" (P. H. Emmett, Ed.). Reinhold, New York, 1955.

3. Mross, W. D., *Catal. Rev. Sci. Eng.* **25,** 591 (1983).

4. Crowell, J. E., Garfunkel, E. L., and Somorjai, G. A., *Surf. Sci.* **121,** 303 (1982); Crowell, J. E., Somorjai, G. A., *Appl. Surf. Sci.* **19,** 73 (1984); Goodman, D. W., *Appl. Surf. Sci.* **19,** 1 (1984); Luftman, H. S., Sun, Y.-H., and White, J. M., *Surf. Sci.* **19,** 59 (1984); Ertl, G., Lee, S. B., and Weiss, M., *Surf. Sci.* **114,** 527 (1982); Praliaud, H., Primet, M., and Martin, G. A., *Surf. Sci.* **17,** 107 (1983); Katzer, J. R., Sleight, A. W., Gajardo, P., Michel, J. B., Gleason, E. F., and McMillau, S., *Faraday Discuss. Chem. Soc.* **72,** 121 (1981).

5. Lackey, D., Surman, M., Jacobs, S., Grinder, D., and King, D. A., *Surf. Sci.* **152/153,** 513 (1985); Broden, G., Hafner, G., and Bonzel, H. P., *Surf. Sci.* **84,** 295 (1979); Sachtler, W. M. H., Shriver, D. F., Hollenberg, W. B., and Lang, A. L., *J. Catal.* **92,** 429 (1985); Alvey, M. D., Lanzilloto, A. M., and Yates, J. T., *Surf. Sci.* **177,** 286 (1986).

6. Nørskov, J. K., Holloway, S., and Lang, N. D., *Surf. Sci.* **137,** 65 (1984); Lang, N. D., Holloway, S., and Nørskov, J. K., *Surf. Sci.* **150,** 24 (1985); S. Holloway, Nørskov, J. K., and Lang, N. D., *J. Chem. Soc. Faraday Trans. I* **83,** 1935 (1987); van Santen, R. A., "Proceedings, 8th International Congress on Catalysis, Berlin, 1984," Vol. IV, p. 97. Dechema, Frankfurt-am-Main, 1984; Ray N. K., and Anderson, A. B., *Surf. Sci.* **125,** 803 (1983).

7. Uram, K. J., Ng, L., and Yates, J. T., *Surf. Sci.* **177,** 253 (1986).

8. Pacchioni, G., Koutecký, J., and Fantucci, P., *Chem. Phys. Lett.* **92,** 486 (1982); Koutecký, J., Pacchioni, G., and Fantucci, P., *Chem. Phys.* **99,** 87 (1985).

9. (a) Durand, Ph., and Barthelat, J. C., *Theor. Chim. Acta* **38,** 283 (1975); (b) Barthelat, J. C., Durand, Ph., and Serafini, A., *Mol. Phys.* **33,** 159 (1977).

10. Serafini, A., Poilblanc, R., Labarre, J. F., and Barthelat, J. C., *Theor. Chim. Acta* **50,** 159 (1978).

11. Pacchioni, G., Fantucci, P., Giunchi, G., and Barthelat, J. C., *Gazz. Chim. Ital.* **110,** 183 (1980); see also Ref. (*9b*).

12. Huzinaga, S. (Ed.), "Gaussian Bases Sets for Molecular Calculations." Elsevier, New York, 1984.

13. Buenker, R. J., and Peyerimhoff, S. D., *Theor. Chim. Acta* **35,** 33 (1975); Buenker, R. J., Peyerimhoff, S. D., and Butscher, W., *Mol. Phys.* **35,** 771 (1978); Buenker, R. J., "Proceedings of the Workshop on Quantum Chemistry and Molecular Physics" (P. G. Burton, Ed.), Woollongong, Australia, 1980; Buenker, R. J., "Studies in Physical and Theoretical Chemistry," Vol. 21. Elsevier, Amsterdam, 1982; Buenker, R. J., and Phillips, R. A., *THEOCHEM* **123,** 291 (1985).

14. Herzberg, G. "Molecular Spectra and Molecular Structure," Vol. I. Van Nostrand–Reinhold, New York, 1950.
15. Heshett, D., Plummer, E. W., de Paola, R. A., and Eberhardt, W., *Phys. Rev. B* **33,** 5171 (1986); Hoffmann, F. M., Hrbek, J., and de Paola, R. A., *Chem. Phys. Lett.* **106,** 83 (1984); Hoffmann, F. M., and de Paola, R. A., *Phys. Rev. Lett.* **52,** 1697 (1984); de Paola, R. A., Hrbek, J., and Hoffmann, F. M., *J. Chem. Phys.* **82,** 2484 (1985); Eberhardt, W., Hoffmann, F. M., de Paola, R. A., Heshett, D., Stratteg, F., Plummer, E. W., and Moser, H. R., *Phys. Rev. Lett.* **54,** 1856 (1985).
16. Arias, J., Lee, J., Dunaway, J., Martin, R. M., and Metin, H. *Surf. Sci.* **159,** L433 (1985).
17. Madey, T. E., and Benndorf, C., *Surf. Sci.* **164,** 602 (1985); Netzer, F. P., Doering, D. L., and Madey, T. E., *Surf. Sci.* **143,** L363 (1984).
18. Wurth, W., Weimer, J. J., Hudeczek, E., and Umbach, E., *Surf. Sci.* **173,** L619 (1986).
19. Müller, W., and Bagus, P. S., *J. Electron Spectrosc. Relat. Phenom.* **38,** 103 (1986).
20. Lambert, D. K., *Solid State Commun.* **51,** 297 (1984).
21. Bauschlicher, C. W., *Chem. Phys. Lett.* **118,** 307 (1985).
22. Kunimatsu, K., Seki, H., Golden, W. G., Gordon, J. G., and Philpott, M. R., *Langmuir* **2,** 464 (1986).
23. Wimmer, E., Fu, C. L., and Freeman, A. J., *Phys. Rev. Lett.* **5,** 2618 (1985).
24. van der Lee, G., Bastein, A. G. T. M., van den Boogert, J., Schuller, B., Luo, H., and Ponec, V., *J. Chem. Soc. Faraday Trans. 1,* **83,** 2103 (1987).
25. Bastein, A. G. T. M., van den Boogert, W. J., van der Lee, G., Luo, H., Schuller, B., and Ponec, V., *Appl. Catal.* **29,** 243 (1987).