Ab Initio Study of the Interaction of Rhodium with Dinitrogen and Carbon Monoxide

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Ab initio computations at the B3LYP/ECP level have been performed on a series of charged and neutral rhodium species containing carbon monoxide and dinitrogen ligands. The computations have been employed to predict possible oxidation states of supported Rh for new surface species detected by infrared spectroscopy during the interaction of the metal with CO and N_2 in the presence of ultraviolet radiation. Specifically, it has been concluded that Rh species containing N_2 ligands giving rise to low-frequency N−N stretching modes most likely contain Rh with a −1 oxidation state, the source of electrons being due to photoinduced electron transfer between supported Rh metal centers in the presence of UV irradiation. Although the computations refer to gas-phase Rh species, it is believed that computations, such as those reported herein, can be useful in predicting trends in vibrational frequencies for similar surface species and thus aid in vibrational band assignments for specific structures.

1. Introduction

There have been numerous experimental studies, primarily utilizing infrared spectroscopy, of the interaction of CO[1] and N_2[2−8] with supported Rh. A limited number of theoretical investigations at various levels of theory on CO/Rh species have also been reported,[9−14] but to our knowledge, N_2/Rh species have not yet been studied by computational procedures. Wovchko and Yates have recently conducted an exciting series of experiments utilizing infrared spectroscopy which concerned the simultaneous interaction of CO and N_2 with Rh/Al_2O_3 under ultraviolet irradiation.[15] Several new surface species were detected in this novel work,[15] which prompted the current theoretical studies.

2. Theoretical Methods

All calculations were made with Gaussian94.[16] Optimized geometries were determined using density functional theory[17−26] with the B3LYP exchange/correlation functional.[27] A 6-311+G(d) basis set was used for carbon, nitrogen, and oxygen while a quasi-relativistic energy-adjusted effective core potential (ECP)[28] was used for the 28 core electrons of rhodium in conjunction with a 6s5p3d basis set contraction (311111/22111/411) for the valence orbitals. This level of theory is denoted B3LYP/ECP.[29]

All species were completely optimized within the appropriate point group. Vibrational frequencies were calculated by taking finite differences of analytical first derivatives.[30] For $Rh(CO)_2$, $Rh(N_2)_2$, and $Rh(CO)N_2$, only the bent geometry was computed because that structure is more likely to be relevant to surface chemistry. On the basis of the observation of only one infrared band for the $^{14}N_2$/Ar matrix, Ozin et al.[31] concluded that $Rh(N_2)_2$ was linear. Pápai et al.[10] computed two structures for $Rh(CO)_2^+$. At the nonlocal density functional level of theory, the bent structure (C−Rh−C, 85.9°) was found to be more stable by 2.1 kcal/mol.

3. Results and Discussion

TABLE 1: Absolute Energies (Hartrees) of Various Rhodium Species

	sym	state (conf)	$\langle S^2 \rangle$	B3LYP/ ECP	ZPC[a]	Cp[b] (298 K)
Rh^+	K_h	$^3F(d^8)$	2.00	−110.217 45	0.00	1.48
Rh	K_h	$^4F(s^1d^8)$	3.75	−110.502 81	0.00	1.48
Rh	K_h	$^2D(d^9)$	0.76	−110.484 89	0.00	1.48
Rh^-	K_h	$^3F(s^2d^8)$	2.01	−110.546 08	0.00	1.48
Rh^-	K_h	$(s^2d^8)^c$		−110.492 73	0.00	1.48
CO	$C_{\infty v}$	$^1\Sigma_g$		−113.349 05	3.16	2.07
N_2	$D_{\infty h}$	$^1\Sigma_g^+$		−109.559 69	3.49	2.07
$RhCO^+$	$C_{\infty v}$	$^3\Delta$	2.00	−223.632 75	4.65	2.79
RhCO	$C_{\infty v}$	$^2\Sigma$	0.75	−223.923 79	4.64	2.67
RhCO	$C_{\infty v}$	$^2\Pi$	0.77	−223.885 71	4.25	2.91
RhCO	$C_{\infty v}$	$^2\Delta$	0.76	−223.927 38	4.62	2.71
$RhCO^-$	$C_{\infty v}$	$^3\Sigma(s^1d^9)$	2.00	−223.947 19	3.98	2.95
$RhCO^-$	$C_{\infty v}$	$^1\Sigma(s^2d^8)$		−223.976 02	4.66	2.58
RhN_2^+	$C_{\infty v}$	$^3\Delta$	2.00	−219.812 84	4.50	3.00
RhN_2	$C_{\infty v}$	$^2\Sigma$	0.75	−220.088 70	4.58	2.83
RhN_2	$C_{\infty v}$	$^2\Delta$	0.76	−220.092 74	4.53	2.89
$Rh(^2\eta\text{-}N_2)$	C_{2v}	$^2A_1$	0.76	−220.072 62	3.65	3.00
RhN_2^-	$C_{\infty v}$	$^3\Delta(s^1d^9)$	2.04	−220.121 57	3.93	3.20
RhN_2^-	$C_{\infty v}$	$^1\Sigma(s^2d^8)$		−220.130 70	4.70	2.68
$Rh(CO)_2^+$	C_{2v}	$^3B_2$	2.01	−337.028 18	9.16	4.42
$Rh(CO)_2^+$	C_{2v}	$^1A_1(d^8)$		−337.031 81	10.24	3.89
$Rh(CO)_2$	C_{2v}	$^2B_2$	0.76	−337.328 87	9.29	4.14
$Rh(CO)_2^-$	C_{2v}	$^1A_1$		−337.411 90	9.22	3.99
$Rh(N_2)_2^+$	C_{2v}	$^3B_2$	2.00	−329.398 65	8.94	4.84
$Rh(N_2)_2^+$	C_{2v}	$^1A_1(d^8)$		−329.366 78	9.78	4.28
$Rh(N_2)_2$	C_{2v}	$^2B_2$	0.76	−329.673 14	8.93	4.62
$Rh(N_2)_2^-$	C_{2v}	$^1A_1$		−329.752 18	9.07	4.40
$Rh(CO)N_2^+$	C_s	$^3A'$	2.00	−333.215 05	9.03	4.65
$Rh(CO)N_2^+$	C_s	$^1A'$		−333.199 62	9.95	4.12
$Rh(CO)N_2$	C_s	$^2A'$	0.76	−333.502 17	9.03	4.43
$Rh(CO)N_2^-$	C_s	$^1A'$		−333.581 90	9.23	4.13

[a] Zero point correction (kcal/mol). [b] Integrated heat capacity (kcal/mol). [c] Not a pure state.

The absolute energies in Hartrees of the various rhodium species and of CO and N_2 considered in this computational study are given in Table 1. The method correctly predicts the ground state of metallic Rh to be the ^4F electronic state with an ionization potential of 7.77 eV, in close accord with the experimental value of 7.46 eV.[32] Also, the ground states of RhCO and $RhCO^+$ are predicted to be $^2\Delta$ and $^3\Delta$, respectively, in agreement with previous CASSCF and MRSDCI computations.[11] A trend which is clear is that the energies of the gas-phase isomeric species are consistently predicted in the order anion < neutral < cation. Thus, the gas-phase species $Rh(CO)N_2^-$ is predicted to be more stable than $Rh(CO)N_2$ by

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TABLE 2: Relative Energies (kcal/mol) of Rhodium Species

	state	elec energy	ΔH(0 K)	ΔH(298 K)
RhCO	$^2\Sigma$	2.2	2.2	2.2
RhCO	$^2\pi$	26.1	25.7	25.9
RhCO	$^2\Delta$	0.0	0.0	0.0
$RhCO^-$	$^3\Sigma$	18.1	17.4	17.8
$RhCO^-$	$^1\Sigma$	0.0	0.0	0.0
RhN_2	$^2\Sigma$	2.5	2.6	2.5
RhN_2	$^2\Delta$	0.0	0.0	0.0
$Rh(^2\eta\text{-}N_2)$	$^2A_1$	12.6	11.7	11.8
RhN_2^-	$^3\Delta$	5.7	4.9	5.4
RhN_2^-	$^1\Sigma$	0.0	0.0	0.0
$Rh(CO)_2^+$	$^3B_2$	2.3	1.2	1.7
$Rh(CO)_2^+$	$^1A_1$	0.0	0.0	0.0
$Rh(N_2)_2^+$	$^3B_2$	−20.0	−20.8	−20.2
$Rh(N_2)_2^+$	$^1A_1$	0.0	0.0	0.0
$Rh(CO)N_2^+$	$^3A'$	−9.7	−10.6	−10.1
$Rh(CO)N_2^+$	$^1A'$	0.0	0.0	0.0

50 kcal mol^{-1} (i.e. an exothermic electron affinity with respect to $Rh(CO)N_2$), and the latter neutral species is more stable than $Rh(CO)N_2^+$ by 180 kcal mol^{-1} (i.e. a positive ionization energy with respect to $Rh(CO)N_2$). Therefore, if the trend noted for the charged and neutral gas-phase species is true for similar species stabilized on a support such as Al_2O_3, one might expect to detect spectroscopically $Rh(CO)N_2^-$ on the surface provided a source of electrons was available.

Numerous experimental studies have established that the oxidation state of Rh is +1 for the rhodium *gem*-dicarbonyl species on metal oxide supports at ambient temperature.[1] The data in Table 1, which show that gas-phase $Rh(CO)_2$ is considerably more stable than $Rh(CO)_2^+$, might seem at first to be in contradiction with experiment.[1] However, one must keep in mind that the calculations refer to real charges while the experimental data are for a rhodium oxide site in which the rhodium has a +1 oxidation state. Correlations of energies of fully charged gas-phase species with energies of transition metal species supported on metal oxides having stabilized oxidation states, i.e. substantial charge delocalization, may be tenuous.[33] Nevertheless, we feel that the trends calculated for CO and N_2 bound to rhodium with different charges should parallel the trend for rhodium in different oxidation states even though a one-to-one correlation of a +1 charge with a +1 oxidation state is not possible.

Table 2 compares the energies of the low-lying electronic states of several of the Rh species considered in this work. It was observed that the $^2\Sigma$ and $^2\Delta$ states for the RhCO and the RhN_2 neutral species were very close in energy such that the true nature of the ground states is in doubt. This was also the case for the $^3B_2$ and $^1A_1$ states of the $Rh(CO)_2^+$ species. However, the difference in energy between the other states tabulated leaves little doubt as to the nature of the ground state for a particular species. Those species containing N_2 tend to have high-spin ground states; the presence of the stronger-field ligand CO tends to induce a preference for a low-spin ground state.

The bond energies predicted by the computations for the CO and N_2 ligands attached to Rh for the various charged and neutral species are shown in Table 3. In all of the gas-phase species the CO ligand was computed to be more strongly bound to Rh than was N_2. This prediction is in accord with all experimental data concerning interactions of CO and N_2 with supported Rh, as CO displaces N_2 from the surface and is much more difficult to remove by evacuation at ambient temperature.[3,6−8] Of the bidentate species in Table 2, CO is bound most tenaciously to Rh in $Rh(CO)N_2^-$. In every case the presence of the N_2 ligand enhances the binding of CO to Rh relative to that in the corresponding *gem*-dicarbonyl species. This is caused by donation of electron density from the N_2 ligand through Rh into the π^* orbital of CO, thus enhancing the σ donation from CO to Rh and increasing the Rh−C bond strength.

Table 4 gives the calculated bond distances and vibrational stretching frequencies for the Rh species considered in this work. The predicted geometries and frequencies are in reasonable accord with those computed previously for RhCO,[10,11,14] $RhCO^+$,[10] $Rh(CO)_2$,[10,14] and $Rh(CO)_2^+$,[10] by *ab initio* methods. As mentioned earlier, the driving force for the current theoretical study was the experimental work by Wovchko and Yates in which several new surface species were postulated on the basis of vibrational frequencies measured by transmission FTIR spectroscopy for Rh/Al_2O_3 in the presence of CO, N_2, and UV irradiation.[15] Table 5 summarizes the experimental data which are currently known for such CO and N_2 interactions with supported Rh.

It is clear from the experimental data in Table 5 that the vibrational frequency corresponding to a C−O stretching mode in a RhCO species decreases in a continuous fashion as the oxidation state of Rh decreases. The same should be true for the N−N stretching mode in RhN_2 species as the negative charge is increased. An examination of the theoretical data in Table 4 reveals that for all cases the vibrational frequencies for the gas-phase RhCO and RhN_2 species are predicted to decrease as the charge is altered from +1 to 0 to −1 in accord with the experimental observations relative to Rh oxidation states. In general, the predicted frequency shifts are considerably more dramatic for the gas-phase species than are those observed

TABLE 3: Bond Energies (kcal/mol) for Rhodium Species

	1st bond energy			2nd bond energy[a]		
	elec	ΔH(0 K)	ΔH(298 K)	elec	ΔH(0 K)	ΔH(298 K)
$Rh(CO)_2^+$	29.1	27.7	28.1	41.6	40.1	40.9
$Rh(N_2)_2^+$	16.4	15.4	15.6	22.4	21.4	22.0
$RhN_2(CO)^+$	14.2	13.3	13.5		same as $RhCO^+$	
$Rh(CO)N_2^+$	33.4	32.0	32.4		same as RhN_2^+	
$Rh(CO)_2$	32.9	31.4	32.0	58.6 (50.7)[b]	57.1 (49.2)[b]	57.9 (50.0)[b]
$Rh(N_2)_2$	13.0	12.1	12.4	30.2 (22.3)[b]	29.2 (21.3)[b]	29.9 (22.0)[b]
$Rh(N_2)CO$	9.5	8.6	9.0		same as RhCO	
$Rh(CO)N_2$	37.9	36.6	37.1		same as RhN_2	
$Rh(CO)_2^-$	54.5	53.1	53.8	84.2 (50.7)[c]	82.7 (49.2)[c]	83.7 (50.2)[c]
$Rh(N_2)_2^-$	38.8	37.9	38.3	49.1 (15.6)[c]	47.9 (14.4)[c]	48.8 (15.3)[c]
$Rh(N_2)CO^-$	29.0	27.9	28.4		same as $RhCO^-$	
$Rh(CO)N_2^-$	64.1	62.7	63.3		same as RhN_2^-	

[a] Bond energies in kcal/mol^{-1} are computed with respect to the rhodium atom or ion in its asymptotic limit. The bond energies in parentheses are corrected to the ground state of the rhodium atom or ion. [b] The values in parentheses have been reduced by 7.9 kcal/mol, which is the experimental separation between the ^2D and ^4F states of rhodium. [c] The values in parentheses have been reduced by 33.5 kcal/mol, which is the computed (B3LYP/ECP) difference between the closed shell singlet rhodium anion in an s^2d^8 configuration and the triplet ground state (^3F).

TABLE 4: Calculated Bond Distances, Bond Angles, and Stretching Frequencies for Ground State Species

		calculated bond distances (Å)					calculated frequencies (cm^{-1})			
	state	Rh−C	Rh−N	C−O	N−N	X−Rh−X (deg)	Rh−C	Rh−N	C−O	N−N
CO	$^1\Sigma_g$			1.128					2213	
N_2	$^1\Sigma_g{}^+$				1.096					2444
$RhCO^+$	$^3\Delta$	1.959		1.123			378		2252	
RhCO	$^2\Delta$	1.832		1.148			511		2085	
$RhCO^-$	$^1\Sigma$	1.740		1.181			609		1888	
RhN_2^+	$^3\Delta$		2.073		1.098			283		2413
RhN_2	$^2\Delta$		1.912		1.112			424		2276
$Rh(^2\eta\text{-}N_2)$	$^2A_1$		2.155		1.135			316		2068
RhN_2^-	$^1\Sigma$		1.792		1.136			550		2092
$Rh(CO)_2^+$	$^1A_1$	1.858		1.127		87.6	473 (s)		2241 (s)	
							441 (a)		2191 (a)	
$Rh(CO)_2$	$^2B_2$	1.881		1.146		101.9	459 (s)		2095 (s)	
							433 (a)		2037 (a)	
$Rh(CO)_2^-$	$^1A_1$	1.851		1.173		128.1	574 (s)		1947 (s)	
							505 (a)		1870 (a)	
$Rh(N_2)_2^+$	$^3B_2$		2.140		1.097	105.9		247 (s)		2420 (s)
								229 (a)		2414 (a)
$Rh(N_2)_2$	$^2B_2$		1.980		1.110	109.8		325 (s)		2293 (s)
								325 (a)		2260 (a)
$Rh(N_2)_2^-$	$^1A_1$		1.891		1.125	169.3		459 (a)		2192 (s)
								446 (s)		2131 (a)
$Rh(CO)N_2^+$	$^3A'$	1.985	2.201	1.124	1.096	107.9	359	211	2236	2427
$Rh(CO)N_2$	$^2A'$	1.860	2.018	1.148	1.107	107.3	470	305	2052	2293
$Rh(CO)N_2^-$	$^1A'$	1.830	1.930	1.172	1.126	145.0	537	414	1911	2153

TABLE 5: Experimental Stretching Frequencies for RhCO, RhN_2, and Mixed Species

postulated structure	postulated oxidation state of Rh	C−O or N−N frequency (cm^{-1})	ref in text
$Rh^{+3}CO$	+3	2136	1d
$Rh^{+2}(O)CO$	+2	2120	1d
$Rh^+(CO)_2$	+1	2096−2102 (s)	1
		2022−2032 (a)	
Rh(CO)	0	2042−2076	1
$Rh^{+\delta}N_2$	$+\delta$[a]	2301−2303	3,5,6
		2270−2276	
RhN_2	0	2248−2257	3,5−8
$Rh(CO)N_2$	−	2048 (C−O)	15
		2234 (N−N)	
$Rh(N_2)_2$	−	2188 (s,a)	15

[a] Oxidized, but to an unknown degree.

(where data are available) for the surface species. Nevertheless, the directional trend appears to be correct. The infraerd studies of Wovchko and Yates based upon isotopic labeling studies unequivocally establish that new vibrational frequencies at 2048 and 2234 cm^{-1} should be assigned to the C−O and N−N stretching frequencies of a $Rh(CO)N_2$ surface species and that a new band at 2188 cm^{-1} should be assigned to a N−N mode of some type of RhN_2 species.[15] The authors were not able to assign definite oxidation states to Rh in these two new surface species. They did, however, point out that their band at 2188 cm^{-1} was identical in frequency to that reported by Ozin and Voet for N_2 interacting with Rh in an Ar matrix at 10 K.[31] Since Rh metal was vaporized directly into the low-temperature matrix, it was assumed that the RhN_2 species contained Rh in the zero oxidation state, and the 2188 cm^{-1} band, which under high resolution was split into two components separated by only 2.5 cm^{-1}, was assigned to a linear $Rh(N_2)_2$ species.[31]

The computations in this work (Table 4) indicate that a $Rh(N_2)_2$ species should give rise to a doublet with its components split by 6 cm^{-1} for the plus-charged species, 33 cm^{-1} for the neutral species, and 61 cm^{-1} for the minus-charged species. It is very unlikely that the new Rh species responsible for the 2188 cm^{-1} band has Rh in the +1 or 0 oxidation states because it is well established (Table 5) that the experimental stretching frequencies for $Rh/N_2^{+\delta}$ and RhN_2 are 2270−2300 and 2248−2257 cm^{-1}, respectively. It would seem more logical that the band observed by Wovchko and Yates refers to RhN_2^- since it has very low frequency and is not split into a doublet. The bands observed at 2048 and 2234 cm^{-1} probably do correspond to Rh in the zero oxidation state since both are close to the established values for RhCO and RhN_2, respectively. A RhN_2^- species is not unreasonable given the conditions of the recent experiment. Ultraviolet irradiation could have caused photoinduced electron transfer[34] between supported Rh atoms in close proximity which may have reduced $Rh(CO)N_2$ to RhN_2^- accompanied by the loss of CO; an adjacent RhCO site could be oxidized to the $Rh(CO)_2^+$ species. Even if the true surface species causing the 2188 cm^{-1} band is a *gem*-dinitrogen one, it would seem that the most likely oxidation state for Rh would still be −1. In this event, it could be postulated that the symmetric component of the expected doublet for $Rh(N_2)_2^-$ would lie under the broad band also corresponding to the N−N stretch in $Rh(CO)N_2$. The 2188 cm^{-1} band observed for a RhN_2 species in a low-temperature matrix was very weak and may not have been due to a $Rh(N_2)_2$ species, as several species $Rh(N_2)_n$, $n = 1-4$, with overlapping band systems were detected.

An alternative interpretation for the 2188 cm^{-1} band is a rhodium site with N_2 bound side-on. We calculate that the $^2A_1$ state of $Rh(^2\eta\text{-}N_2)$ is a minimum, though less stable than the the $^2\Delta$ state of RhN_2 by 11.8 kcal/mol (Table 2).[35] Although the computed N−N stretching frequency of the $^2A_1$ state (2068 cm^{-1}, Table 4) is too low, the band corresponding to it is predicted to be quite intense (297 km/mol). We were unable to optimize a $Rh(CO)N_2$ species with N_2 bound side-on. Perhaps the photolytic preparation of the surface enhanced a rhodium site for side-on binding of N_2.

In conclusion, we believe that *ab initio* computations of properties of gas-phase transition metal ions and molecules can be useful in at least predicting trends in experimental observations for surface species. Specifically, we believe that the calculations in this study suggest that Rh could exist in a −1 oxidation state upon interaction with CO and N_2 mixtures in the presence of ultraviolet photons which could cause photoinduced electron transfer.

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