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Surface Oxidation of Some Rh(I) Compounds and Some Polymer-Supported Rh(I) Catalysts

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Several Rh(I) compounds used in homogeneous hydrogenation and isomerization catalysis, and some of their heterogenized derivatives have been investigated by the X-ray photoelectron spectroscopy (XPS) technique. XPS measurements both on polymer-bound rhodium complexes, and on mononuclear Rh(I) complexes with monomeric ligands taken as reference compounds and used as precursors in the preparation of heterogenized catalysts, as well as some other Rh complexes structurally similar to such precursors, show, from Rh 3*d* spectra, the presence of several oxidation states of rhodium (i.e., +1 and higher), the higher oxidized being generally the major component in the surface layers. The extent of the oxidation phenomenon increased with time and was dependent on the structure and nature of ligands (e.g., $RhCl(CO)(PPh_3)_2$ being the most stable toward surface oxidation).

INTRODUCTION

Heterogenized catalysts prepared by implantation of Rh(I) complexes on organic polymers containing N, P, or $-COO^-$ donor functions, have shown particularly high activity and selectivity in processes of hydrogenation or isomerization of olefins under mild conditions (*1–3*). Their activity as heterogenized catalysts is often different from that of the parent Rh(I) complexes, when used in homogeneous catalysis (*1, 2*), and possibly related changes in surface structure and composition have been observed (*1, 3*).

Interest in surface properties of heterogenized Rh(I)-based catalysts already synthesized and catalytically investigated by some of us (*1–3*) prompted us to attempt a surface characterization of some such catalysts by X-ray photoelectron spectroscopy (XPS). The investigation was extended to simple Rh(I) complexes, and was actually more intensively focused on the latter, since they turned out to be subject to similar surface changes in the solid state, and the assessment of such structural effects is simpler in solids of well-defined bulk composition than in polymer-anchored systems of variable stoichiometric composition.

In a previous investigation (*4*) we found evidence for the presence of oxidized species on the surface of the Wilkinson compound $RhCl(PPh_3)_3$ in the solid state under real conditions, and hypotheses on the nature of these species were proposed, also on the grounds of the study of their reactivity in the solid state. In the present work we extended our investigation to further rhodium(I) compounds currently used in homogeneous catalysis, and to some heterogenized derivatives; all these systems were prepared as Rh(I) species, but they often showed the occurrence of surface oxidation products in the solid state, while retaining Rh(I) character in the bulk.

There are many previous literature reports on the reactivity of Rh(I) complexes in solution toward dioxygen (*5–9*), whereas less attention has been paid up to now to the behavior in the solid state (*1, 10*); however, a better knowledge of the chemical behavior of Rh(I) solid compounds would be relevant from the catalytic point of view. One can indeed expect that formation of contaminating surface species during the

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storage of the complexes, such as have been observed in Ref. (*11*), can modify the catalytic properties of rhodium species, not only in heterogeneous processes, but also when used in the homogeneous phase. Even if surface oxidation products are likely to be reduced during catalytic hydrogenation processes, they are possible precursors of formation of catalytic sites, and can therefore influence activity and dispersion of the true active species.

On the other hand, the low concentration of these contaminants, which is probably of "catalytic" order of magnitude and restricted to the surface layers since the bulk composition is still close to pure Rh(I), need a highly specific analytical technique to be revealed. The XPS technique appears therefore particularly well suited for such investigation, in view of its ability to provide information about oxidative phenomena on the surface of solid samples.

The nature of the surface oxidation products has already been discussed in the previous note (*4*) for the Wilkinson compound; among various possible hypotheses, such as formation of either paramagnetic rhodium(II) or diamagnetic rhodium(III) complexes resulting from oxidative addition, the most plausible one for the oxidized species on $RhCl(PPh_3)_3$ surface appeared to be essentially consistent with the formation of Rh(III) species, and we shall discuss in the present paper the possible extension of the same interpretative scheme to further related rhodium species.

EXPERIMENTAL

Rhodium compounds were prepared according to literature methods and characterized by elemental analysis and by their chemical and physical properties. The investigated species include the simple compounds $RhH(PPh_3)_4$ (*1*), $RhH(CO)(PPh_3)_3$ (*1*), $Rh[Me_2(CH)COO](PPh_3)_3$ (*1*), $RhCl(CO)(PPh_3)_2$ (*12*), $RhCl(PPh_3)_3$ (*13*), $RhCl(PCy_3)_2$ (*14*), $RhCl_2(PCy_3)_2$ (*15*), and $Rh(OH)(CO)(PPh_3)_2$ (*16*), as well as heterogenized products prepared by implantation of $RhH(PPh_3)_4$ and $RhH(CO)(PPh_3)_3$ complexes on benzylvinyl ether/maleic acid alternating copolymer, as described in previous literature reports (*3, 17*).

Satisfactory elemental analysis, at the same level of accuracy as given in the original reference were found for all the above simple compounds. The following are reported as examples: $RhH(CO)(PPh_3)_3$: C(72.0%), H(5.2%), Rh(11.6%), P(9.9%); $RhCl(CO)(PPh_3)_2$: C(69.5%), H(4.6%), Cl(3.7%), Rh(10.9%), P(9.7%); $Rh[Me_2(CH)COO](PPh_3)_3$: C(70.7%), H(5.41%), Rh(11.0%), P(10.05%). For the heterogenized systems, whose elemental composition may vary according to the degree of loading of the rhodium compound, data were in agreement with the original papers (*3, 17*). For example, quantitative data for $RhH(PPh_3)_4$ supported on BVE/Mac (BVE/Mac = benzylvinyl ether/maleic acid alternate copolymer, 05/05) were: C(56.6%), H(5.14%), P(4.75%), Rh(9.7%), P/Rh (1.63%), –COOH/Rh(4%) (Ref. (*3*)).

Syntheses were usually performed with no particular care of air exclusion, except for PCy_3 derivatives, which are far more air-sensitive than other compounds investigated here, and were therefore prepared under Ar atmosphere. Handling of samples after synthesis was performed deliberately under "real" conditions including exposure to air, except for the PCy_3 species, which decompose very rapidly on exposure to air (*14*) and which were therefore to be handled always under argon of 99.998% purity. The XPS study was performed on a VG-ESCA 3 electron spectrometer equipped with a cylindrical electrostatic analyzer. All spectra (samples were dusted as thin films onto gold-bearing plates) were obtained with $AlK\alpha_{1,2}$ radiation (1486.6 eV). Oil diffusion pumps fitted with cold traps produced a vacuum better than 10^{-8} Torr, typically between 5×10^{-9} and 5×10^{-10} Torr. Calibration was made by the $4f_{7/2}$ gold signal at 84.0 eV (with full width at half-maximum FWHM ca. 1.8 eV), and sample charging (usually in the range 1 to 2 eV) was corrected for by assuming the binding energy (b.e.) of the C 1*s* line to be 285.0 eV; in most compounds investigated here the main source of C 1*s* ionization are phenyl C atoms of the $\mathrm{PPh_3}$ ligands, whose b.e. is usually assumed to be very close to, if not coincident with, that of "contamination carbon" and therefore used as reference (e.g., Refs. (*10, 18–20*)). In the $\mathrm{PCy_3}$ derivatives as well we assumed, for want of an alternative reference, the phosphine carbon signals to be at 285.0 eV, so a larger experimental uncertainty is to be expected in this case. The reproducibility of the b.e. value was always within ±0.1 eV, and the accuracy of the measured binding energies was estimated as ±0.2 eV. FWHM of XPS signals are reported in parentheses. Bands of composite shape and with particularly large FWHM values, containing signals from different kind of atoms of the same element, were resolved into components of Gaussian shape, assuming FWHM values corresponding to single signals (usually 1.8 eV for Rh $3d_{5/2}$). The ESR measurements were carried out as previously reported (*1*).

RESULTS

a. XPS Measurements

Table 1 reports the binding energies and FWHM in eV for core lines of rhodium compounds. Some rhodium compounds were observed to be sensitive to X irradiation after prolonged exposure. In order to minimize errors arising from decomposition of the samples, irradiation times as short as possible were used and several measurements were carried out on samples ob-

TABLE 1

Binding Energies (eV) of Rh 3*d*, P 2*p*, Cl 2*p* Levels for Rh Compounds

Compound	Rh $3d_{5/2}$	P $2p_{\mathrm{av}}$	O 1*s*	Cl $2p_{\mathrm{av}}$
$\mathrm{Rh^{I}Cl(CO)(PPh_3)_2}$	308.9 (2.0)	131.7 (2.2)	533.0 (3.1)	198.8 (3.1)
$\mathrm{Rh^{I}Cl(PPh_3)_3}$	308.0 (2.3)–309.7 (2.3)	132.1 (3.0)	531.9 (3.0)[c]	199.1 (3.7)
$\mathrm{Rh^{I}(OH)(CO)(PPh_3)_2}$	309.0 (2.8)	131.7 (3.0)	532.3 (3.5)	—
$\mathrm{Rh^{I}H(PPh_3)_4}$	309.4 (2.6)	132.6 (2.5)	531.4 (3.0)[c]	—
$\mathrm{Rh^{I}Cl(PCy_3)_2}$	308.1 (2.4)–309.5 (2.4)	131.8 (3.2)	531.9 (3.5)[c]	198.8 (3.6)
$\mathrm{Rh^{I}H(CO)(PPh_3)_3}$ (fresh)	308.7 (2.1)	131.6 (2.5)	532.3 (3.3)	—
$\mathrm{Rh^{I}H(CO)(PPh_3)_3}$ after 6 months from preparation	309.5 (3.7)	131.7 (2.9)	532.4 (3.4)	—
$\mathrm{Rh^{I}[Me_2(CH)COO](PPh_3)_3}$	307.4 (2.3)–309.9 (2.4)	131.9 (3.0)	531.8 (3.0)	—
$\mathrm{Rh^{I}(BVE/Mac)}$[a]	309.6 (3.0)	132.4 (2.6)	532.4 (3.3)	—
$\mathrm{Rh^{I}(CO)(BVE/Mac)}$[b]	309.7 (3.5)[d]	132.4 (3.1)	532.4 (3.4)	—
	307.1 (2.5)–309.8 (2.8)[e]	132.8 (3.0)	532.4 (2.6)	—
$\mathrm{Rh^{II}Cl_2(PCy_3)_2}$	309.2 (2.0)	131.1 (2.4)	532.3 (3.2)[c]	198.9 (3.1)
$\mathrm{[Rh^{II}(CH_3COO)_2]_2}$	309.0 (2.1)	—	531.9 (2.5)	—
$\mathrm{Rh^{III}Cl_3 \cdot 3H_2O}$	310.2 (2.0)	—	533.2 (2.9)	199.6 (3.2)
$\mathrm{Rh^{III}Cl_3(PPh_3)_3}$	310.0 (2.5)	132.3 (3.1)	531.9 (3.1)[c]	199.4 (3.4)

Note. FWHM in parentheses. All samples in "real" conditions, i.e., in air before XPS measurements, except the $\mathrm{PCy_3}$ derivative (see text). Rh $3d_{3/2}$ signals (not reported in detail) occurred at 4.7-eV higher b.e. and showed the same (composite) patterns as Rh $3d_{5/2}$.

[a] Heterogenized complex obtained from $\mathrm{RhH(PPh_3)_4}$ and the benzylvinyl ether/maleic acid alternating copolymer.

[b] Heterogenized complex obtained from $\mathrm{RhH(CO)(PPh_3)_3}$ and the above ligand.

[c] Weak O 1*s* signal from pump oil contamination.

[d] Real product.

[e] After four reaction cycles in the isomerization and hydrogenation of pent-1-ene at 50°C in benzene as reaction medium, $P_{\mathrm{H_2}}$ = 100 kPa.

tained from different preparation runs. Usually, spectra were recorded in the first 30–40 min of exposure of samples to X-rays (typically 12 kV × 5 mA through an Al window of 0.04 mm thickness). Cooling of the sample to liquid N_2 temperature was also performed in some cases as an additional precaution against possible secondary decomposition effects, which, however, turned out to be negligible.

In order to establish preliminarily a possible classification of the oxidized species on the surface of Rh(I) complexes, we assumed that actual b.e. values depend both on the oxidation state and on the chemical environment of Rh (through additive ligand effects), i.e., $\text{b.e.} = (\text{b.e.})_{o,n} + \Sigma_{\text{ligand}}\ \Delta\text{b.e.}(\text{ligand})$.

As typical central values we assumed, both from our own measurements and from literature reports obtained with similar referencing procedures, the following $(\text{b.e.})_{o,n}$ values as typical for rhodium in its various oxidation states:

Rh $3d_{5/2}(\text{b.e.})_{o,n}$ (eV)

-Rh(0): 307.1 – (pure metal)
-Rh(II): 309.0 – (e.g., $[Rh(CH_3COO)_2]_2$)
-Rh(III): 310.0–310.2 – (e.g., $RhCl_3 \cdot 3H_2O$–$RhCl_3(PPh_3)_3$).

By interpolation, the Rh $3d_{5/2}(\text{b.e.})_{o,1}$ value should fall around 308.1 eV for Rh(I); for pure species, containing one kind only of Rh atoms, the FWHM under our experimental conditions is expected to be not larger than ca. 1.8 eV. On the contrary, experimentally we usually obtained signals which were either doubled, or in any case broader than 1.8 eV, and shifted to higher b.e. values (see Fig. 1).

For $RhCl(PPh_3)_3$ (*4*) and $Rh[Me_2(CH)COO](PPh_3)_3$, Rh $3d_{5/2}$ XPS spectra are particularly complex, and show two full-grown components, the former falling in the range 307.5–308.5 eV, and the latter between 309.0 and 310.2 eV. For $RhH(PPh_3)_4$ and $RhCl(PCy_3)_2$ the spectra show mainly the patterns of several oxidation states of rho-

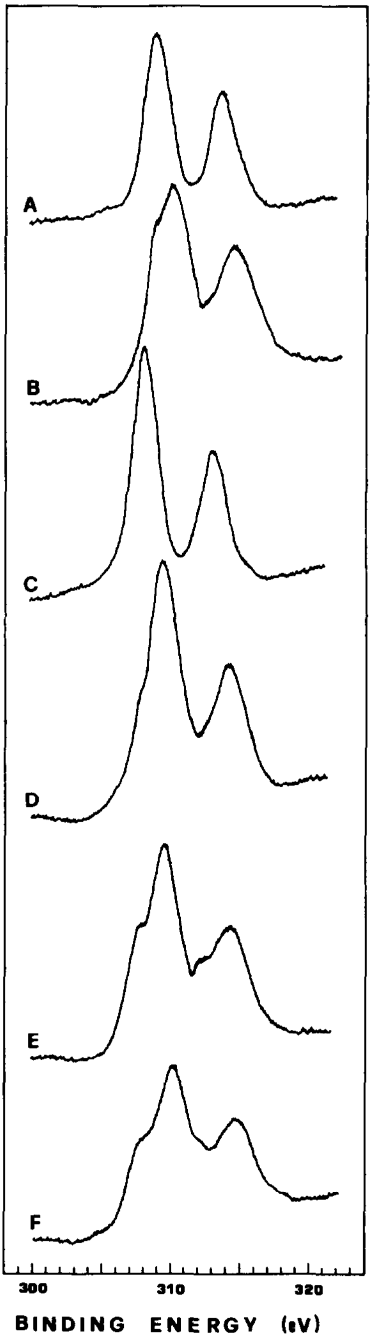

FIG. 1. XPS spectra of Rh $3d$ level for rhodium compounds: (A) $RhH(CO)(PPh_3)_3$ fresh; (B) $RhH(CO)(PPh_3)_3$ after 6 months from preparation; (C) $RhCl(PCy_3)_2$ (Rh(I) species in the fresh compound); (D) $RhCl(PCy_3)_2$ after air exposure (see text); (E) $RhCl(PPh_3)_3$ under real conditions of air exposure (cf. Ref. (*4*)); (F) $Rh[Me_2(CH)COO](PPh_3)_3$ under real conditions.

dium with only a small amount of Rh(I). Rh $(OH)(CO)(PPh_3)_2$ and $RhH(CO)(PPh_3)_3$, exposed for a long time to the air, give a broad signal with FWHM values of 2.8 and 3.7 eV (*10*) and b.e. values at 309.0 and 309.5 eV, respectively.

b. Surface Oxidation in Rh(I) Compounds: Effect of Ligands

All the prepared Rh(I) complexes had elemental bulk composition satisfactory for the desired compound as already reported and discussed in the Experimental section. Synthetic procedures and purification were carried out so as to ensure formation of only one species of purity ≥99% (*1*). The presence of contaminating rhodium species with oxidation number higher than 1, as revealed by XPS, and thus in much higher abundance in the surface layer sampled by XPS, has therefore to be considered mainly or exclusively as a consequence of surface oxidation; this surface oxidation may also have been present since the original synthesis of the compounds, and have escaped bulk analysis (see below).

The amount of oxidized species of the surface was different for different compounds, increasing in the following approximate order:

$$\begin{aligned} &\mathrm{RhCl(CO)(PPh_3)_2} < \mathrm{RhCl(PPh_3)_3} \\ &\qquad < \mathrm{Rh[Me_2(CH)COO](PPh_3)_3} \\ &\quad < \left\{\begin{matrix}\mathrm{Rh(OH)(CO)(PPh_3)_2}\\ \mathrm{RhH(CO)(PPh_3)_3}\end{matrix}\right. < \left\{\begin{matrix}\mathrm{RhH(PPh_3)_4}\\ \mathrm{RhCl(PCy_3)_2}\end{matrix}\right. \end{aligned}$$

Binding energy values for the Rh(I) component in the complex Rh $3d_{5/2}$ spectra of the examined complexes lie on the average around 308.2 eV; however, the individual values are actually scattered over a quite large interval. This can be accounted for by contributions from the substituents (Table 2), which to a first approximation were assumed to be additive, and can be represented by a series of ligand parameters. In Table 2 we propose two possible choices (a and b) for such parameters, both of which fit satisfactorily the experimental results of the present work.

TABLE 2

Contribution of Ligand Parameters to Binding Energy (b.e.) of Rh(I)

$(b.e.)_{o,n}$ (eV)	Substituent contribution to b.e. (eV)					
	Cl	O	CO	H	P	5-Coord.
(a) 308.0	(a) +0.9	+0.4	+0.6	+0.4	−0.3	+0.5
(b) 308.2	(b) +0.7	+0.3	+0.3	+0.3	−0.3	+0.4

Binding energy values for Rh $3d_{5/2}$ in Rh(I) species recalculated with the above ligand contributions (a) and (b) are compared with measured b.e. values in Table 3.

It is noteworthy that the effect of different ligands in the above Rh(I) systems causes an overall dispersion of binding energies (ca. 1.4 eV) similar to that reported for Rh(III) compounds (*21*). It follows that, depending on the type and number of the ligands, differences in b.e. values for Rh(I) may be higher than those corresponding to a variation in the oxidation number itself.

On the other hand, data reported by different authors for the same rhodium compound often cover a considerably wide range of values (0.3–1.0 eV) (*11, 18–22*) which is larger than expected from the use of different instruments and/or referencing procedures (*11, 18–20, 22*).

The observed b.e. values are, on the average, higher than the range expected for Rh(I), and are therefore indicative of the presence of Rh species in oxidation states higher than the nominal value +I. Such species could be present since the original synthesis and manipulation of the compounds carried out in air, and not detected by bulk analysis since they are likely to be confined to a thin surface layer. In particular for $RhCl(PPh_3)_3$ and $RhH(CO)(PPh_3)_3$, the very broad peaks obtained with FWHM of 3.4 and 3.2 eV, respectively, by the authors (*10, 21*) under similar resolution conditions as the present work, suggest that the spectra are indicative of the presence of

TABLE 3

Measured b.e. Values for Rh(I) $3d_{5/2}$ Compared with b.e. Recalculated with the Ligand Contributions (a) and (b), Reported in Table 2

b.e. (eV)	$RhCl(CO)(PPh_3)_2$	$RhCl(PPh_3)_3$	$Rh[Me_2CHCOO](PPh_3)_3$	$Rh(OH)(CO)(PPh_3)_2$	$RhH(CO)(PPh_3)_3$	$RhH(PPh_3)_4$	$RhCl(PCy_3)_2$
Measured	308.9	308.0	307.4	308.2	308.8	307.9	308.1
Recalculated (a)	308.9	308.0	307.5	308.4	308.6	307.7	308.3
(b)	308.6	308.0	307.6	308.2	308.4	307.8	308.3

more oxidation states, even though this phenomenon was not pointed out in the cited papers.

$RhCl(PPh_3)_3$, when handled in reducing atmosphere, shows only one single narrow Rh $3d_{5/2}$ signal at the b.e. value expected for Rh(I), whereas it gradually turns into mixtures with more highly oxidized species after exposure to oxygen-containing atmosphere (see Ref. (*4*)). An extreme case is represented by $RhCl(PCy_3)_2$ which is much more sensitive to air exposure and shows the low b.e. spectrum typical of Rh(I) only when freshly synthesized in oxygen-free conditions (spectrum C in Fig. 1); very low levels of O_2 exposure (ca. 10^6 Langmuirs at room temperature) produced rapid and almost complete formation of surface oxidized species (spectrum D in Fig. 1), which is also visible through the color change from the pink–violet of the nonoxidized Rh $Cl(PCy_3)_2$ to the sand-yellow of the oxidized species. As for the compounds examined in the present work, structural data available from the literature are fewer than for Wilkinson compound, so we have even less data to help establish hypotheses on the nature of the surface alterations. However, the general similarity of XP spectral patterns allows us to assume that parallel trends occur in surface reaction mechanisms and that spectral components, observed at higher b.e. values, are therefore due to labile adducts with molecular oxygen, containing rhodium(III) as already observed for $RhCl(PPh_3)_3$ (*4*). Actually, interaction with O_2 starting from Rh(I) precursors could in principle lead also to complexes where the dioxygen ligand is arranged in a superoxo geometry, in which case the formal oxidation state of rhodium can be interpreted as either (II) or (III) (*9, 23*). The former alternative is expected to correspond to a paramagnetic structure which is not of general occurrence and appears to be supported only in a few cases by ESR detection of paramagnetic species (*1*).

In our previous note (*4*) we reported an XPS investigation carried out comparatively on Wilkinson compound $RhCl(PPh_3)_3$ and the Bennett adduct with molecular oxygen $RhCl(O_2)(PPh_3)_3 \cdot 2CH_2Cl_2$, where evidence was obtained for substantial similarity between the oxidized species on the surface of Wilkinson compound and the Bennett species, the former being possibly modified and made more reactive by dispersion on the surface. For the above analogy, the same type of structure can be reasonably assigned also to the oxidized species reported in the present paper; possibly, more than one outer monolayer is involved in such oxidation process, which requires a corresponding rearrangement of the crystal and molecular structure in the outermost layers of the Rh catalyst. If we push forward the structural analogy discussed above, it would appear correct to formulate our oxidized compound on the basis of available X-ray structural data (*24, 25*) as a Rh(I) species; however, XPS data, also on the grounds of possible correlation to additive chemical shift contributions from the ligands, appear indicative of a situation in which the metal atom is in an oxidation state higher than one and quite close to the typical b.e. values of Rh(III) systems.

In the case of the heterogenized Rh(I)

complexes coordinated to the polymeric matrix through the carboxylate groups of the side-chains, the real catalysts Rh(BVE/Mac) and Rh(CO)(BVE/Mac) show predominantly the presence at the surface of oxidized rhodium species (Table 1). The latter system, examined after four catalytic cycles, exhibited some significant changes in the XP spectrum. The decrease of b.e. values of $3d_{5/2}$ levels indicate that the starting oxidized rhodium species undergo a substantial conversion into reduced species (final b.e. = 307.1 eV). The latter b.e. value is affected by additional uncertainty because of the presence of additional C species in the polymer-bound sample, and consequent possible shift of the C 1*s* b.e.; however, the trend between oxidized and reduced species and a comparison with the values obtained for $Rh[Me_2(CH)COO](PPh_3)_3$, a suitable low-molecular-weight model of comparable coordination environment, lead us to the conclusion that these reduced species can be formulated as Rh(I) derivatives. Assignment to the metal oxidation level is possible after repeated cycles leading to irreversible reduction.

This finding is in agreement with the previously demonstrated lability of the oxidized surface species and confirms that the XPS technique, on the basis of appropriate comparative data, may be a powerful tool for the study of the changes taking place in catalytic hydrogenation systems.

DISCUSSION

The analogy in XP spectral patterns suggests that the structure of the oxidation products generally found in almost all solid Rh(I) compounds which we examined (both mononuclear precursors and heterogenized species) is similar to that observed in our previous comparative examination of the Wilkinson and Bennett compounds (*4*). The surface oxidation reaction involves most probably an expansion of the coordination sphere of rhodium, which is likely to produce distortions in the stereochemical arrangement around the Rh atom, and consequently may contribute to increase the reactivity of the species.

The formal oxidation state of the oxidized species is not yet definitively assigned, as previously mentioned (*4*), although several different hypotheses about molecular oxygen Rh(I) adducts and Rh(III) peroxo derivatives have been proposed in previous literature (*23, 26*).

XPS data, although unable by themselves to solve completely the problem, provide an indirect support to the hypothesis of Rh(III) species, since Rh $3d_{5/2}$ b.e. values are relatively high and fall outside the usual range for normal Rh(I) species which are generally reported to be around 308 eV under comparable experimental conditions (*11, 18–21*). We are led therefore to conclude that reactions of Rh(I) species with molecular O_2 produce a rather profound perturbation on the electronic structure of rhodium, which becomes no longer comparable to that of the Rh(I) precursor compounds and does not allow a clear and unequivocal definition of the formal oxidation state. XPS evidence yields quantitative data to emphasize that the perturbation of the Rh(I) system, caused by oxygen adduct formation, produces a deeper perturbation of the electronic structure than could be inferred on the basis of the crystallographic bond length data in the coordination environment.

Moreover, XPS provides a useful experimental method to follow surface changes in solid samples of rhodium(I) compounds which are not easy to detect by other techniques. The observed changes in the electronic structure are accompanied by the formation of new species; in a previous report (*4*) such species have been characterized, on XPS evidence, as being rapidly and easily decomposed under mild conditions (e.g., the oxygenated species are decomposed by treating with H_2 at low pressure and 100°C (*4*)).

XPS measurements allow a preliminary assessment of the chemical behavior of such surface products and of the considerable differences from the precursor species.

Such experimental findings are a contribution toward a more systematic knowledge of the solid-state reactivity of Rh(I) species, which will ultimately result in a better understanding of their catalytic activity.

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