Inorganica Chimica Acta, 44 (1980) L139–L141
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X-ray Photoelectron Spectra of Some Dirhodium Carboxylate Complexes

A. M. DENNIS, R. A. HOWARD, K. M. KADISH, J. L. BEAR*

Department of Chemistry, University of Houston, Houston, Tex. 77004, U.S.A.

J. BRACE[a] and N. WINOGRAD[b]

Department of Chemistry, Purdue University, W. Lafayette, Ind. 47907, U.S.A.

Received October 8, 1979

During recent years there has been considerable activity in elucidating the chemical reactions and measuring the physical properties of tetra-μ-carboxylatodirhodium(II) complexes (hereafter referred to a rhodium(II) carboxylates) [1–6]. Of special interest is the determining of the extent of metal–metal interaction and the bond orders of these complexes [4, 5, 7–9]. The fact that they form stable 1:1 and 2:1 axial adducts with a wide variety of ligands has resulted in several investigations dealing with the degree of σ and π bonding involved [1, 3–5]. The recent work by Christoph and co-workers [4] on the effect of σ and π bonding axial ligands on Rh–Rh bond distances has posed a number of questions with regard to bond orders predicted by the various orbital energy tables that have been proposed [7–9], as well as to the extent of π bonding to axial ligands at the rhodium(II) centers.

Recently we reported the electron transfer properties of an extensive series of rhodium(II) carboxylates, $Rh_2(O_2CR)_4$ [10] in both aqueous and nonaqueous media. In almost all solvents rhodium(II) carboxylates were found to undergo a one-electron reversible oxidation to $[Rh_2(O_2CR)_4]^+$, the exact potential being dependent on the substituent, R, and the nature of the solvent. The electrochemical results of our laboratory [10] and others [3, 11] indicate that the half wave potential for the oxidation of the neutral metal dimer is affected by the σ and π bonding ability of the axial ligand. Strong σ bonding ligands decrease the potential whereas π acceptor ligands tend to increase the potential.

The purpose of the research reported in this paper was to measure the X-ray photoelectron spectra of the neutral rhodium(II) dimer, $Rh_2(O_2CCH_3)_4$, its oxidation product, $[Rh_2(O_2CCH_3)_4]^+ClO_4^-$, and the monoadduct of the neutral complex where the axial ligand is a π acceptor. It was anticipated that this data would answer questions with regard to the equality of the two rhodium centers in $[Rh_2(O_2CCH_3)_4]^+$ and the monoadduct $[Rh_2(O_2CCH_3)_4$(4-cyanopyridine)], as well as furnish information about the electron density distribution within the different complexes.

Experimental

Chemicals

All solvents and organic chemicals were of the highest purity available from Aldrich Chemical Co., Milwaukee, Wis., and were used without subsequent purification. Rhodium(II) acetate, purchased from Matthey Bishop Inc., Malvern, Pa., was recrystallized from acetone before use. Rhodium(II, III) acetate was synthesized from the rhodium(II) precursor by the method previously described by Moszner and Ziolkowski [12]. The 4-cyanopyridine monoadduct of rhodium(II) acetate was prepared by heating the bisadduct in vacuum at 150 °C until the monoadduct was formed. The loss of one 4-cyanopyridine required approximately 30 min under these conditions.

X-Ray Photoelectron Spectroscopy

The XPS spectra were recorded on a Hewlett-Packard 5950A spectrometer at the ambient probe temperature of 300K, using monochromatized Al Kα X-ray radiation. The spectrometer system and sample preparation used have been previously described [13, 14]. Charging of insulating compounds was minimized by preparing thin sample films that enabled photoelectrons from the gold substance to be readily detected [14, 15]. This procedure has been applied successfully elsewhere [14, 16]. Since it is difficult to establish a valid external reference energy level for insulators [15] we have chosen the C 1s peak as a convenient internal reference for all binding energies reported, and have assigned to C 1s the value of 284.5 eV. Any differences observed in the binding energy of the C 1s electrons due to contaminant hydrocarbons, will be very small [15]. With the use of the flood gun of the XPS spectrometer we observed that all photopeaks from a given insulating sample were shifted by the same amount (within the error of measurement), when the induced positive surface charge was reduced by very low kinetic energy electrons. Quoted binding energies relative to the C 1s standard are reproducible to a precision of ± 0.1 eV.

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*Author to whom correspondence should be addressed.

[a] Present address: Physique des Liquides et Electrochimie, Université de Paris VI, 4, Place Jussieu, Tour 22, Paris, France.

[b] Present address: Department of Chemistry, Pennsylvania State University, University Park, Pa. 16802.

TABLE I. Binding Energies for Selected Rhodium Compounds[a].

Compound	Rh $3d_{5/2}$	Rh $3p_{1/2}$	O 1s	C 1s[b]
$RhCl_3 \cdot 3H_2O$	309.9	–	–	–
NaO_2CCH_3	–	–	530.7	288.1
Rh metal	306.1	–	–	–
$Rh_2(O_2C(CH_2)_2CH_3)_4$	308.4	522.6	531.6	287.8
$Rh_2(O_2CCH_3)_4$	308.5	522.7	531.7	287.8
$Rh_2(O_2CCH_3)_4(4CNpy)$[c]	308.2	522.3	531.4	287.5
$[Rh_2(O_2CCH_3)_4]^+ClO_4^-$	310.1	523.8	532.2	288.1

[a] Binding energies referenced to C 1s = 284.5. [b] Binding energy of carboxyl carbons. [c] N 1s = 399.3 eV.

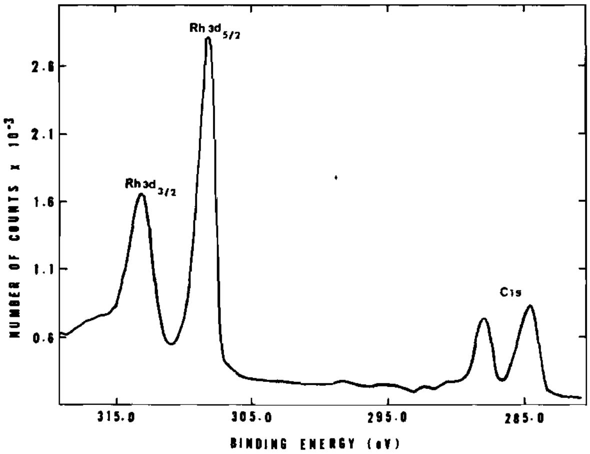

Fig. 1. X-ray photoelectron spectra of $Rh_2(O_2CCH_3)_4$ between 280 and 320 eV. The C 1s peak at 287.8 eV is due to the four acetyl carbons while that at 284.5 is of the four methyl carbons.

Results and Discussion

The X-ray photoelectron spectrum of $Rh_2(O_2CCH_3)_4$ is shown in Fig. 1. Binding energies for $Rh_2(O_2CCH_3)_4$ and its oxidation product $[Rh_2(O_2CCH_3)_4]^+ClO_4^-$ are listed in Table I. Also listed in this table are the binding energies for a number of other reference rhodium compounds. For both the neutral compound, $Rh_2(O_2CCH_3)_4$, and the oxidized complex, $[Rh_2(O_2CCH_3)_4]^+ClO_4^-$, only a single Rh $3d_{5/2}$ peak is observed, implying that there exists identical rhodium atoms in each dimeric complex within the time scale of the XPS measurement. The Rh $3d_{5/2}$ binding energy of the oxidized complex is shifted from 308.5 eV to 310.1 eV, consistent with the increase of positive charge in converting Rh(II) to Rh(II 1/2). An increase of 0.5 eV of the O 1s binding energy was also observed upon oxidation, indicating strong interaction of the bridging carboxylates with the two rhodium atoms. Again, only a single O 1s peak is observed, suggesting equivalent oxygen atoms and implying equivalency of the two rhodium atoms to which they are bound.

The O 1s binding energy for NaO_2CCH_3 is lower than that of rhodium(II) acetate and butyrate by 0.9 to 1.0 eV and rhodium(II, III) acetate by 1.5 eV. As expected, the increased positive environment produced by Rh(II) and Rh(II 1/2) decreases the electron density of the carboxylate oxygens. However, a similar trend is not observed for the carboxylate C 1s binding energy. In fact there is a 0.3 eV decrease in the C 1s binding energy for rhodium(II) acetate and butyrate. One possible explanation for the increase in electron density on the carboxylate carbons is donation of electron density from the filled δ orbital of the Rh_2^{4+} framework or system into the empty π^* orbital of the carboxylate species. Any donation of electron density would be concentrated on the carboxylate carbon because of the large π coefficient. This interpretation is consistent with Christoph's findings [4, 5] where he proposes a strong rhodium–carboxylate π interaction to explain the short rhodium–rhodium distance and also, the longer than expected C–O bond distance. Another indication of a strong π interaction is the Rh $3d_{5/2}$ binding energy for Rh(II 1/2) which is even larger than that observed for rhodium(III) chloride.

The 4-cyanopyridine monoadduct of rhodium(II) acetate exhibits lower binding energies than those displayed by the parent dimer. If extensive back bonding from the rhodium(II) center into the π system of the pyridine ring exists, one would expect to see a decrease in electron density on the rhodium ions. It is apparent that the σ interactions with the weakly basic ring nitrogen of 4-cyanopyridine are still sufficient to offset any putative loss in electron density through back bonding.

In conclusion, it appears that within the sensitivity of the experimental method, the electron density on both of the two rhodium ions in $[Rh(O_2CCH_3)_4]^+ClO_4^-$ and $Rh_2(O_2CCH_3)_4$(4-cyanopyridine) is identical in each case. The results also indicate the existence of a rhodium carboxylate π interaction but no measurable rhodium 4-cyanopyridine π interaction.

Acknowledgements

We wish to acknowledge support of this work by the Robert A. Welch Foundation (KMK-Grant E 680), (JLB-Grant E-196), the National Institutes of Health (JLB) and the National Science Foundation (N.W.). We also acknowledge the help of Marie-Claude Hayoit de Termicourt with some of the XPS spectra.

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