Electronic Structures of Organo-Transition-Metal Complexes

I. Silver(I)-Olefin Complexes

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Received February 19, 1973

By using the closed-shell SCF-MO method with the CNDO type approximation for all valence electron systems, the electronic structures of some Ag⁺-olefin complexes are investigated. The calculated values of $-\Delta H$ increase with the increasing number of methyl groups on the double bond and this trend agrees with the experimental result. Also calculation reproduces many experimental results, such as the infrared, Raman, and $^{13}$C NMR spectra. These experimental results are discussed on the basis of the calculated electronic structures of Ag⁺-olefin complexes.

Key words: Ag⁺-olefin complexes

1. Introduction

Many transition metal complexes catalyze certain reactions [1], such as isomerization, dimerization, polymerization, oxidation, hydrogenation of olefins and acetylenes. A number of organo-transition-metal complexes have been synthesized and investigated using various methods [2], because these complexes were interesting as models of the intermediates of such reactions.

The Ag⁺-olefin complex [3] is one of the well known organo-transition-metal complexes, and its thermodynamic and spectroscopic studies have been carried out; heretofore equilibrium constants of the formation [4–7], enthalpies of formation [4, 6, 7], infrared [8, 9], Raman [9] and nuclear magnetic resonance (NMR) spectra [9–12] have been measured.

Since Dewar proposed the two-way donor acceptor bond in the silver-olefin complexes, some theoretical studies have been carried out on the natures of coordination bond in such complexes; the perturbation method has been applied for the estimation of the stability of Ag⁺-olefin and Ag⁺-aromatic compound complexes [8, 14–17] and molecular orbitals (MO) of Ag⁺-ethylene have been obtained by the extended Hückel and ab initio MO methods [18, 19]. However there seems to have been no reports of systematic MO calculations on a series of Ag⁺-olefin complexes, and theoretical interpretations of the experimental results, such as the infrared, Raman and NMR etc., are rather scarce. Thus, the author will calculate the MO's of six Ag⁺-olefin complexes by the semi-empirical SCF-MO method, and present some discussions on the experimental results from the obtained MO's in this paper.
2. Calculation and Geometry

The SCF MO's are obtained by the CNDO type MO method, which has been applied to the MO calculations of MnO\textsubscript{2}, CrO\textsubscript{2}\textsuperscript{2-}, PdX\textsubscript{2}\textsuperscript{2-} and PdX\textsubscript{6}\textsuperscript{2-} (X = halogen) in a previous work [20].

All valence orbitals including 4d-atomic orbitals of the silver atom are considered explicitly. The zero-differential overlap approximation [21] is introduced into the Roothaan's SCF equation for the closed shell molecules [22]. Then the diagonal one-electron term $H_{rr}$ in the Fock matrix element is evaluated according to the formula of Yonezawa et al. [23]$^1$. The off-diagonal one-electron term $H_{rs}$ ($r \neq s$) is calculated by the Wolfsberg-Hermholz approximation [24],

$$H_{rs} = -kS_{rs}(I_r + I_s)$$

(1)\footnote{While the one-center exchange integrals are included in the formula of Yonezawa et al., the author neglects them in this calculation.}

where the parameter $k$ is taken as 0.55. The one-center Coulomb repulsion integrals of ligand atoms are obtained by the Pariser's approximation [25] and those of the silver atom are taken from the Oleari's report [26]. The two-center Coulomb repulsion integrals are computed according to the Ohno's formula [27]. The single Slater type orbital is used for all s- and p-orbitals, and the double-$\zeta$ form is used only for the 4d-orbitals of the silver atom. The values of the orbital exponents $\zeta_r$, ionization potentials $I_r$, and one-center Coulomb repulsion integrals $(rr|rr)$ are given in Table 1.

The core-repulsion energy $E_{\text{nucl}}$ is approximated by:

$$E_{\text{nucl}} = \sum_{A} \sum_{B} \sum_{r} \sum_{s} N_r N_s (rr|ss)$$

(2)\footnote{For the notations used in these formulas, see Ref. [23].}

Table 1. Orbital exponents ($\zeta_r$), valence state ionization potentials ($I_r$) and one-center Coulomb repulsion integrals $(rr|rr)$

| Atom | AO | $\zeta_r$ | C$^a$ | $I_r$ (eV) | $(rr|rr)$ (eV) |
|------|----|-----------|------|-----------|-------------|
| H    | 1s | 1.0000 [31] |      | 13.60 [33] | 12.85 [33] |
| C    | 2s | 1.5679     |      | 21.07     | 12.10       |
|      | 2p | 1.5679     |      | 11.27     | 10.93       |
|      |    | 2.6130     | 0.6701 |           |             |
|      | 5s | 2.1900     |      | 7.07      | 7.46        |
|      | 5p | 2.1900     |      | 3.30      | 6.22        |

$^a$ The 4d-atomic orbital is represented by Basch et al. [32] as the linear combination of one 3d and two 4d Slater orbitals. In this work, the contribution of 3d Slater orbital is neglected and the 4d-atomic orbital is represented as the linear combination of two 4d Slater orbitals. Therefore strictly speaking, this 4d-atomic orbital is not normalized. However the contribution of the 3d Slater orbital is negligible small and the error induced by this approximation is very small, e.g., less than 0.2% in the case of the overlap integral between the silver atom and the carbon atom.