Some problems of catalytic selectivity and geometrical changes of coordinated ligands caused by pseudo Jahn–Teller's effect

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Abstract

Three different theoretical approaches were used for the study of the geometry changes of some coordinated organic ligands. It was shown that the quantum-chemical calculations with variation of the interatomic distances of these ligands may serve as a good approximation for the adequate description of the pseudo Jahn–Teller's effect (PJTE) in them. The theoretical results of these calculations and the one parametric theory of the vibronic activation are in a good agreement with the known experimental data. The ability to describe the geometry changes, caused by coordination, opens a new way for the explanation of the selectivity of catalytic action. The last problem is very important for various needs of homogeneous catalysis. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

It is known that the coordinated molecule (ligand) changes its geometry due to the variation of its electronic and nuclear configuration by its coordination in different complexes of transition metals and on solid surfaces [1]. These changes may be investigated both direct quantum-chemical calculations and different experimental methods (for instance, X-ray methods) [2]. However, these methods meet various practical difficulties by their realization for concrete chemical systems, they are usually oriented to the study of stabilized systems. The main part

of intermediates can not be described by means of them. Thus, it is interesting to find some general regularities of the interaction between an active centre (AC) and a reagent (R) basing on their electronic properties. As will be shown in the present work, these properties allow us to predict the changes of electronic and nuclear configurations of the investigated reagent by its coordination. The geometry distortions of allene ($CH_2=C=CH_2$), acetylene (C_2H_2) and its derivatives [$R-C\equiv C-R$, where R = H, CN, Ph, $C(CH_3)_3$] are observed in various complexes of transition metals, including some complexes of platinum (0) with ethylene. Such situation is known also for the complex of W(0): $[W(CO)(C_2H_2)]^0$, in which the distance be-

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tween two carbon atoms of acetylene is equal to 1.30 Å. At the same time, this metal forms some acetylene complexes, which have $R_{cc} = 1.50$ Å, and even 1.69 Å.

The planar nuclear configuration of C_2H_4 is distorted for its complexes. For example, two CH_2 groups form the torsion angle H−C−C−H, which equals to 90° (the case of $[Fe(CO)_4 C_2H_4]^0$).

The electronic state of free ethylene has the same geometry, when one of its π-electrons is excited onto its LUMO [3]. The kind of coordination mentioned is typical for different complexes with low oxidation degrees of metals or for surfaces of metal solids. This fact is connected with their ability for back π-donation [2,4]. As it was shown by us on the basis of the one-parametrical theory of vibronic activation (OTVA), its usage gives the values of charge transfers Δq_i together with the values of activation energy changes of the double bond. The investigation of the activation of C_2H_4, C_2D_4, C_3H_6 and $C_2H_mF_n$ ($m + n = 4$) is presented for the complexes, given in Table 1. By this method we can study the changes of different geometrical parameters of coordinated molecules [4,5].

In the present work, we offer the simple rules given below, which avoid the above-mentioned difficulties.

The principal circumstance connected with any catalytical reaction is the independence of geometrical distortion of small molecules on the way of population of its free molecular orbitals (MO), which are able to participate in the following pseudo Jahn–Teller's effect (PJTE), causing its introduction into the investigated reaction. Hereafter, we shall call this principle ''the principle of independence'' for the investigated catalytical reaction.

From our point of view, the best catalyst for the investigated catalytical reaction, which requires the known type of geometrical distortion of small molecule under the investigation, must fit the requirements given below.

(1) It must take place on the maximal approximation of the energy values of its highest occupied MO to the degenerated energetical value of the MO of the small molecule.

(2) By the forming the complex of this small molecule with the best catalyst, the preliminary transition of the electronic density of the catalyst onto its free MO is to be accompanied by the small changes of its geometry. The last changes must be near to the values of its interatomic distances, which correspond to the degeneration of its free (vacant) MO.

(3) When these interatomic distances are reached, the population of these free MO will take place. The population will cause the PJTE of the small molecule, leading to its essential distortion, which is required for its introduction into the investigated catalytical reaction.

(4) Bearing in mind the above-mentioned principle of independence, we consider that steps (1)–(3) may be realized just the same by means of the action of photons.

2. Theory

Other possibilities for the analysis of the electronic structures and nuclear configurations may be obtained by means of quantum-chemical calculations, taking into account the variation of interatomic distances of free ligands. Another way of solving this problem is the usage of the PJTE. The latter gives us the possibility to describe the interaction (mixture) of the basic electronic state of the free ligand with its ex-

Table 1
Orbital charge transfers to HOMO Δq_1 and LUMO Δq_2 and reduction ΔE of the activation energy E of C_2H_4 for the intermediates $[NiX_2C_2H_4]^n$ and $[PtCl_3C_2H_4]^-$

System	ΔR	Δq_1	Δq_2	$\Delta E / E_0$ ($E_0 = 86$ kcal/mol)
$[Ni(PH_3)_2C_2H_4]^{2+}$	0.019	−0.35	0.16	0.24
$[NiC_2H_4]^{2+}$	0.623	−0.42	0.15	0.26
$[NiF_2C_2H_4]^0$	0.015	−0.23	0.17	0.20
$[Ni(CN)_2C_2H_4]^0$	0.054	−0.84	0.03	0.38
$[PtCl_3C_2H_4]^-$	0.206	−0.18	0.97	0.56

cited ones on the basis of its vibrations, which have the corresponding symmetry. Such investigations, which were done by us using the variation of interatomic distances and the PJTE, allow to explain the geometry changes in the case of the distances C=C and C−Cl for C_2H_4 and C_2H_3Cl. These geometry changes were discussed for the coordination of these molecules with ACs, formed by different transition metals. At the same time, these methods are able to show some particularities of the electronic cloud redistribution of these systems by their coordination, connected with the nature of ACs. The geometry changes of the investigated reagent by its coordination may serve as a key for the better understanding of such principal catalytic property as selectivity [2,4,6]. The geometry of the coordinated ligand, changed due to its coordination, causes the disturbance of its MO. The latter guarantees the presence of the overlap maximum between these MO and the MO of the AC under consideration.

The general selectivity requirement is the choice of such ACs, which give the needed geometry and hence the corresponding electronic distribution of coordinated ligands. Here it is to distinguish two different cases, describing monomolecular and bimolecular reactions. Their orbital symmetry rules were formulated in [7].

Monomolecular reactions (i.e., bonds' breakings, and different bonds' regroupings in coordinated ligands) are allowed in accordance with molecular symmetry, if their catalytic perturbation potential contains the representation of the direct product $\Gamma_{k\alpha} \otimes \Gamma_Q \otimes \Gamma_{1\alpha}$. Here, k$\alpha$ and 1α are the interacting MO, which are mixed by means of the molecular vibration of Q-type. The orbital symmetry rules require the condition, given below, for bimolecular reactions, which form the majority of all catalytic reactions. Their catalytic perturbation potential must contain the representation of the direct product $\Gamma_{(HOMO)\alpha} \otimes \Gamma_{(LUMO)\beta}$. However, the forecast ability of these rules is low, as it was noted in the work [7]. It is due to the absence of the knowledge about the

form of the catalytic potential. The main aim of our present article is to avoid this difficulty. Bearing in mind the last circumstance, we consider electronic structures of different reagents and products define the requirements to electronic structures of possible ACs. The difference between two electronic structures, belonging to the free ligand and its coordinated form, respectively, defines such molecular parameters of the sought AC as its geometry, the position of its energy levels, its bonds' hardness and so on. In other words, this difference allows us to describe the further chemical behaviour of this ligand by its coordination.

3. Results and discussion

Considering the cases of C_2H_4 and C_2H_3Cl, we have approximated the electronic state of these coordinated molecules (Fig. 1) by means of variations of their two interatomic distances C=C and C−Cl. Our calculations were done on the basis of the MINDO method [8–10]. Calculations using an ab initio package GAMESS [11] gave analogous results. The influence of the following distances: C=C for C_2H_4, C=C and C−Cl for C_2H_3Cl on their MO are given in Figs. 2 and 3, respectively. The conclusion, given below, follows from the comparison of the geometrical parameters of coordinated C_2H_4 and C_2H_3Cl and their electronic structures
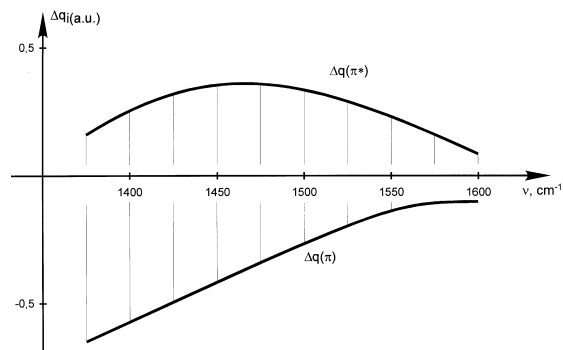

Fig. 1. Correlation diagram for the quantities $\Delta q_{\pi}(\nu)$, $\Delta q_{\pi}^*(\nu)$, where ν is the vibration frequence of coordinated molecule C_2H_4.
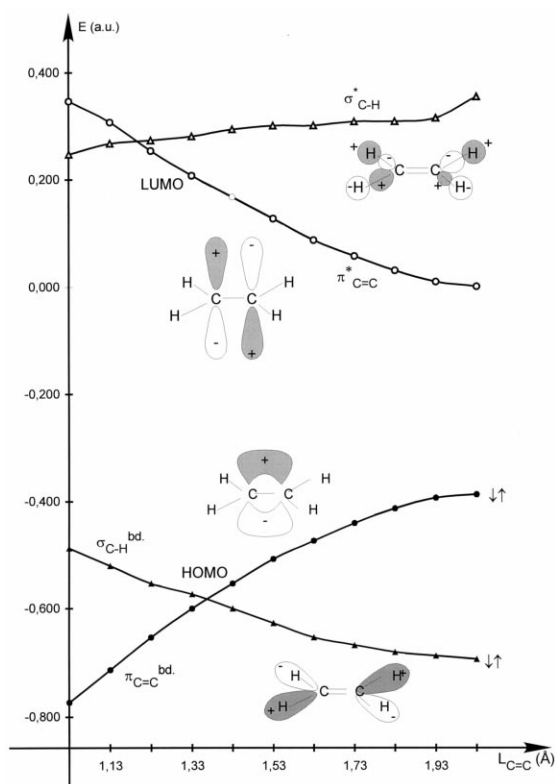
Fig. 2. Energy levels' and MO changes for C_2H_4 vs. its distance C=C.

[1,12]. The electronic structures of these coordinated molecules may be described by using the electronic structures of their free forms. The latter must be calculated with the interatomic distances, which coincide with the same distances for the coordinated forms of these molecules. We consider the electronic structure of artificially deformed molecules copies the electronic structure of the same coordinated ones. These deformed molecules appear (and it is a principal question) quasi-excited electronic states [1–4,13]. Such molecules may be described by means of linear combinations of their MO, belonging to their free undeformed forms. Any of these combinations is formed due to one molecular ground state and one or more of its excited MO. This situation was obtained by us theoretically using the OTVA approximation and really was observed experimentally [2,4,13]. Really, the increase in the interatomic distances

C–C for C_2H_4 and C_2H_3Cl influences both the change of their electronic levels' states and the nature of the MO, corresponding them. The HOMO and the LUMO are π-orbitals of this C–C bond at the large values of interatomic distances. The latter belong to the region of interatomic distances for the coordinated forms of these molecules. The MO of σ-type, which is built by means of the atomic functions of C and Cl atoms, remains the LUMO, when the increase in the distance C–Cl for C_2H_3Cl takes place. The bonds' orders for these systems change essentially by the variation of their interatomic distances (see Table 2).

It is to note that direct quantum-chemical calculations are usually impossible because of the absence of any information about the geometrical structure of systems AC–R. It follows from the nature of these complex systems, considered as intermediates. The geometrical data sets for such systems may be obtained on the basis of the EXAFS method and by means of
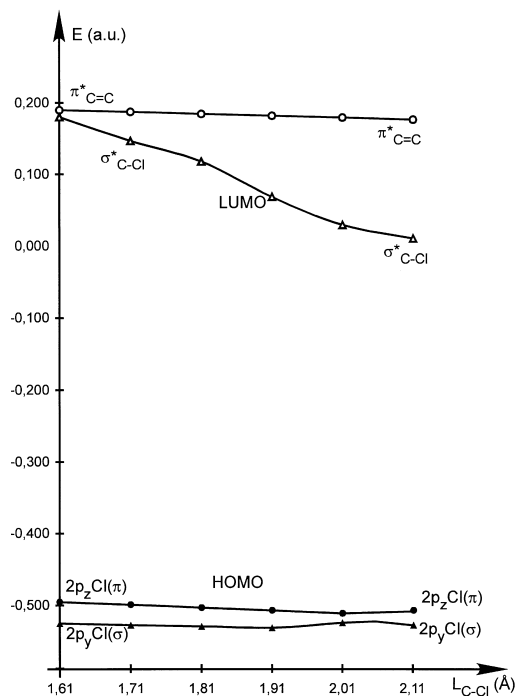

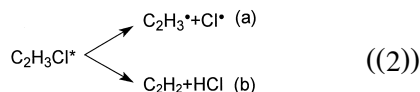Fig. 3. Energy levels' and MO changes for C_2H_3Cl vs. its distance C–Cl.

Table 2
Interatomic distances (Å), atomic charges (a.u.), bonds' orders and full energies (a.u.) for the ground and the first excited states of C_2H_3Cl

$R(C_1=C_2)$	$R(C_2-Cl)$	$R(C_1-H)_{trans}$	$Q(C_1)$	$q(C_2)$	$R(C_1=C_2)$	$R(C_1-Cl)$	$R(C_2-H)_{trans}$	E_{total}
1.33	1.71	1.08	0.105	−0.054	2.059	0.930	0.950	−34.41576
1.73	1.71	1.08	0.075	−0.090	1.938	1.018	0.983	−34.03152
1.33	2.11	1.08	0.095	−0.041	2.090	0.871	0.933	−34.25000
								$(S = 0)$
1.33	1.71	1.08	−0.089	−0.070	1.903	0.404	0.856	−34.15897
1.73	1.71	1.08	−0.008	−0.068	1.001	1.073	0.982	−33.71050
1.33	2.11	1.08	−0.121	−0.015	2.050	0.190	0.898	−33.89302
								$(S = 1)$

the IR and Raman's spectroscopy, too [2]. The results of our calculations let us to explain the photochemical behaviour of C_2H_3Cl. Its photochemical reaction takes place at the wavelengths $\lambda = 190 \div 220$ nm. This fact meets the experimental confirmation [15,16]. It is supposed that this process has two stages:

$$C_2H_3Cl \overset{h\nu}{\to} C_2H_3Cl^* \qquad (1)$$

and then

$$C_2H_3Cl^* \begin{cases} C_2H_3^{\bullet} + Cl^{\bullet} \quad (a) \\ C_2H_2 + HCl \quad (b) \end{cases} \qquad ((2))$$

The analysis of the results, presented in Fig. 3 and in Table 2, shows that, from the theoretical point of view, such behaviour of C_2H_3Cl is most possible by the light influence on it. We used our method for the analysis of the photochemical behaviour of different complex systems. For instance, this method was used successfully for the analysis of the photochemical properties of various amino-complexes of transition metals, belonging to the triodes: Fe–Ni, and Os–Pt [17,18]. The good agreement with the experimental data was obtained for both the descriptions of the photochemical behaviour of the complexes and their ligands' free forms. It indicates the adequate description of their photochemical behaviour by means of the above-mentioned scheme, which is based on the approach of so-called ''frozen'' MO and on the Franc–Condon's principle [17]. The experimentally observed ratio of the ways (a) and (b) for the stage (2) — C_2H_3/C_2H_2 is equal to 1.41. The way (a) becomes more preferable than the (b) one by this condition (see Fig. 3). The bond C⋯C of the coordinated C_2H_4 is half-loosened for the intermediates $NiX_2C_2H_4$ (where X = PH_3, F^-, CN^-) with respect to the double bond of this free molecule [14]. The value of the length C–C is more for the coordinated state, than in the case of free C_2H_3Cl molecule.

The similar situation is observed (as a rule) for photo-excited coordination compounds [17,18]. It is clear that for both these cases, the electronic state of the investigated ligand in its coordinated or photo-excited forms is adequate to its electronic state, received by means of the calculations on the basis of different changes of its geometry. The theory of the PJTE is the basis for this conclusion.

Let us consider the case of the interaction of C_2H_4 with light. Its electronic state A_{1g} is the ground electronic state. Its electronic distribution is $\pi^2\pi^{*0}$. The first electron-excited state is $^1B_{1u}$ with the electronic distribution $\pi^1\pi^{*1}$. One excited electron occupies its unbonding orbital of π^*-type. The ligand configuration, containing two CH_2-groups, forming the torsion angle 90°, is the most stable configuration for this case. The geometry of coordinated state is average between the planar configuration of free C_2H_4 and the above-mentioned one. The distor-

tion degree depends on the nature of metal and the nature of other ligands in the AC. In other words, the choice of the AC is regulated by this degree. The PJTE describes such geometrical configurations of intermediates as well [1,13]. It takes place by the mixture of the ground and excited states due to the vibration of B_{1u}-type. Thus, the discussion of all the possible cases of the interaction of ground and excited states of free molecules (because of the PJTE) gives us the possibility to predict their electronic structures, and hence, their geometry for their coordinated forms [17,18]. The degree of the influence of the AC on the reagent is defined by its possibility to include one or more electron-excited states of R into the process of the chemical bonding for the coordination in the joint system AC–R. It is natural that the R influences on the AC by its coordination. However, this influence is weaker due to the large dimensions of the latter as compared with the R.

4. Conclusion

Thus, our calculations, taking into account the changes of interatomic distances and modelling the geometry changes, caused by the PJTE, are very effective for the investigation of electronic structures of reagents by their catalytic coordination process. These calculations may be used for the prediction of various ways of catalytic reactions as well.

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