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Quantum-chemical Study of the Coordination Influence upon the Acetylene Acidity. Intermediate State of the Reaction of Acetylene Oxidative Dimerization

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The influence of π-coordination with copper upon the acidity of substituted acetylenes has been studied. The effect of the formal charges of the metal and ligands as well as that of the complex structure were considered. Linear and dimeric models of the synchronous electron transfer from acetylene fragments to copper atoms with simultaneous formation of a C–C bond for the reaction of acetylene oxidative dimerization have been explored.

Introduction

When discussing the reactions catalyzed by ions of transition metals, the conception is widely used of an essential influence of coordination upon chemical properties of ligands, in particular, their acidity. However, direct quantitative experimental data on such an influence are rather scarce even for stable complexes. Moreover, they are unavailable for weak complexes, the formation of which during reactions is often postulated. Therefore, it is interesting to elucidate this influence on the basis of theoretical quantum-mechanical calculations. It has been shown [1, 2] that the CNDO method can be successfully applied to the analysis of the effect of substitution on the acidity of CH acids. We have used the same method [3] to interpret available experimental data on the acidity of coordinated water molecules, *viz.* that of hydrate and hydrate–ammonium complexes of transition metals of the iron group. The influence of the metal charge and type as well as the ligand type on water acidity has been studied. The fundamental importance of the donor–acceptor interaction was shown. The results obtained give hope that this method can be also used to analyze the acidity of more complex coordinated ligands, *e.g.* acetylenes. In principle, it also allows studying other reaction stages, *e.g.*, those associated with the electron transfer from a ligand to a metal.

In this work the above aspects are considered for reactions of acetylene dimerization in the presence of Cu(II) ions. The mechanisms of acetylene reactions catalyzed by transition metal ions are today under intensive experimental study. Most investigated is the reaction of oxidative dimerization of acetylenes. In ref. 4 the following 3-stage scheme of oxidative dimerization mechanism has been proposed:

$$\mathrm{Cu(II)_s + RC{\equiv}CH \overset{k_1}{\rightleftarrows} Cu(II)RC{\equiv}CH + S} \qquad (1)$$

$$\mathrm{Cu(II)RC{\equiv}CH \overset{k_2}{\rightleftarrows} Cu(II)RC{\equiv}C^- + H^+} \qquad (2)$$

$$\mathrm{2Cu(II)RC{\equiv}C^- \xrightarrow{k} R(C{\equiv}C)_2R + 2Cu(I)} \qquad (3)$$

The first stage is exclusion of a ligand from the coordination sphere of copper by the acetylene, the second one is dissociation of the coordinated acetylene, while the third stage is a synchronous act of electron transfer from the acetylene fragments to copper atoms with a simultaneous formation of C–C bond. This scheme was proved for dehydrodimerization of acetylenes in buffered solution in the absence of O_2 and univalent copper. For other conditions this mechanism requires further evidence. It has been concluded [5, 6] that the reactivity of acetylenes is symbatic with their acidity. A model dimeric structure of a four-center intermediate complex has been proposed [5, 6].

In the present work the CNDO method has been applied to investigation of the second and the third stages of dehydrodimerization reaction. The calculations were performed using the unrestricted Hartry–Fock method in the CNDO approximation. The parametrization [7] for the metal and that [8] for ligand atoms have been used. For free acetylenes the geometry [9] was utilized.

In coordinated acetylenes the length of C–C bond was assumed to be 1.27 Å, as in complexes with platinum, while the other bond lengths were considered as unchanged. If not stated otherwise, the octahedron π-complex of acetylene with copper was a distorted octahedron in which the molecule of substituted acetylene was located perpendicularly to the long diagonal with Cu–C distance being 2 Å, while 5 aqualigands were in the octahedron vertices with Cu–O distance being 2.19 Å and 2.05 Å [10] (see Fig. 1a). The model included the 3d and 4s orbitals

TABLE I. Comparison of Deprotonation Energies ΔE for Noncoordinated and Coordinated Substituted Acetylenes.[a]

RH≡CH R	Free Acetylenes		Coordinated Acetylenes			
	ΔE (eV)	q_H	r = 2 A		r = 2.25 A	
			ΔE (eV)	q_H	ΔE (eV)	q_H
CH_3	−0.338	0.051	−15.03	0.151	−13.99	0.138
H	0.000	0.047	−15.55	0.148	−14.45	0.135
CH≡C	−0.45	0.057	−14.77	0.154	−13.75	0.142
CH_2Cl	−0.68	0.049	−15.05	0.146	−14.03	0.134
CF_3	−1.59	0.041	−16.07	0.139	−15.03	0.125

[a] ΔE for free acetylene equal to 34.43 eV is assumed to be a zero point.

TABLE II. Dependence of the Deprotonation Energy on the Structure of $Cu^{+2}(H_2O)_5(CH{\equiv}CH)$ Complex.*

Structure	*a*	a_1	*b*	b_1	*a'*	*a''*
ΔE (eV)	−15.55	−14.52	−15.65	−14.51	−14.45	−13.44

*a, a_1, b, b_1 structures are designated according to Fig. 1. a' is structure a with r(Cu–C) = 2.25 Å; a'' is structure a with r(Cu–C) = 2.5 Å; ΔE of free acetylene is taken as a zero point.

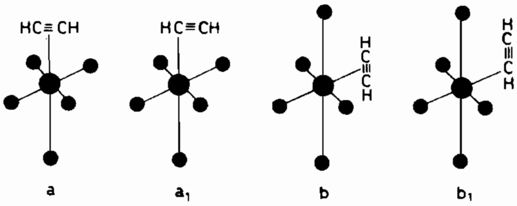

Fig. 1. Structure of $Cu^{+2}(H_2O)_5(CH{\equiv}CH)$ complex.

of the metal, all valent orbitals of the substituted acetylene and one sp^3-hydrid orbital of each aqua-ligand.

Acidity of Acetylenes

The left side of Table I presents the deprotonation energy in the gas phase (ΔE) calculated by us for three substituted acetylenes as well as charges at acetylenic hydrogen. The deprotonation energies give a qualitatively correct reflection of the acidity growth in this sequence, correlating with the Taft constants σ^* [11]. Methylacetylene, for which the value of ΔE is underestimated (consistent with [12]), is an exception. Hydrogen charges correlate with ΔE only for three last acetylenes in accordance with [2].

Table II presents the dependence of the acetylene deprotonation energy on the structure of the complex $Cu^{+2}(H_2O)_5(CH{\equiv}CH)$ (the structures are shown in Fig. 1). It can be seen that the deprotonation energy differs negligibly for the acetylene coordination along the long octahedron diagonal (structure *a*) and the short one (structure *b*). The acetylene shift with respect to the symmetry axis of the complex results in a more noticeable variation of ΔE. The largest effect is obtained by variation of the distance Cu–C. Its increase from 2 Å to 2.5 Å is accompanied with the growth of ΔE by 2 eV. It is also interesting to trace the variation of spin properties of the complex with changing Cu–C distance. For structure a with r(Cu–C) = 2 Å and 2.25 Å, the unpaired electron is located mainly at the $3d_{z^2}$ orbital of copper. When the distance increases to 2.5 Å, it moves to the $3d_{x^2-y^2}$ orbital as in square complexes of copper.

On the right side of Table II, the gas-phase deprotonation energies and the proton charges are given for substituted acetylenes of the complex with Cu^{+2} at two distances Cu–C (2 Å and 2.25 Å). It can be seen that the coordination with Cu^{+2} increases the acidity, this increase being several times larger than the scale of the substitution influence on the acidity of free acetylenes. It also follows from the table that the acetylene itself becomes more acid, whereas diacetylene, chloromethylacetylene and trifluoronemethylacetylene do not change their position in the acidity sequence. The abnormal behaviour of acetylene can be due to imperfection of the CNDO method used. However, it cannot be excluded that the coordination influences the position of substituted acetylenes in the acidity sequence. The same effect may arise because of the difference in the structure of the complex with substituted acetylenes.

TABLE III. Variation of the sp-Hybrid Orbital Population, Wiberg Index P, Overlap Population Q and the Total Energy with the Distance r in the Linear Model of an Intermediate Complex (see Fig. 2a).

Bond r (A)	sp-Orbital population	C_2–C_2'		C_1≡C_2		C_1≡C_2 Cu		E_{tot} (eV)
		P	Q	P	Q	P	Q	
1.5	0.9398	1.021	1.564	2.4387	2.6580	0.8686	1.5968	−3853.4613
2.0	1.0505	0.8036	0.7682	2.5078	2.6677	0.9133	1.6638	−3840.6496
2.5	1.3381	0.3465	0.2306	2.5123	2.6394	1.0422	1.7564	−3833.4852
∞	1.7718	–	–	2.4911	2.5892	1.0965	1.9090	−3840.5984
[a]	1.9135	–	–	3.0048	3.0348	–	–	

[a] Free HC≡C⁻ ion.

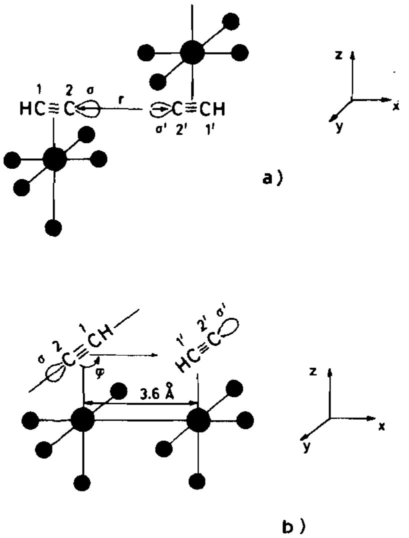

Fig. 2. Intermediate stage models for the oxidative dimerization of acetylene: (a) linear, (b) dimeric; (σ) sp-hybrid orbital.

The Influence of the Charges of the Metal and Ligands

As in the case of σ ligands [3], the acidity increases with the charge of the metal cation. If, for example, ΔE of non-coordinated acetylene is taken to be zero, then for a complex with Cu^{+1} (at r_{Cu-C} = 2 Å) ΔE ~ −8 eV, while for a complex with Cu^{+2} (r_{Cu-C} = 2 Å) ΔE ~ −15 eV. Besides, in the complex with Cu^{+1}, the Cu–C distance is considerably larger due to the difference of covalent radii of Cu^{+1} and Cu^{+2} (0.2 Å [13]), hence ΔE increases. The introduction of charged ligands into the complex also influences the acetylene acidity. For instance, if three chlorine anions are present in the first coordination sphere of Cu^{+2}, ΔE is of the order of 1 eV, *i.e.*, the coordination does not affect the acidity; in a similar complex with Cu^{+1} it leads to a considerable decrease in the acidity. By comparing the scale of ΔE variation due to the complex structure (~1 ÷ 2 eV) and that due to the charge ($Cu^{+1} \rightarrow Cu^{+2}$, δΔE ~ 7 eV), one can see that the charge effect is much stronger. For example, for the complex of propargyl alcohol with Cu^{+1}, the variation of the complex structure (coordination by C≡C bond only, by C≡C bond and oxygen, a shift of the acetylene molecule along C≡C bond) results in a ΔE variation of about 0.5 eV at ΔE = −7.6 eV, whereas the increase of the complex charge, *i.e.*, the formation of the complex with Cu^{+2}, varies ΔE by 7.4 eV.

Calculations of the Intermediate State in the Reaction of Oxidative Dimerization of Acetylene

For the synchronous electron transfer from an acetylene fragment to a copper atom with a simultaneous formation of C–C bond, two models have been considered: (1) linear (two molecules of coordinated acetylide ion come together along X-axis, Fig. 2a); (2) dimeric (HC≡C⁻ fragments rotate around $\text{Cu}-\overset{\text{C}}{\underset{\text{C}}{|||}}$ bond in a rigid dimeric complex with Cu^{+2} in which copper atoms are bound by acetate bridges, Fig. 2b).

For the linear model, the variation of the total energy, atomic charges and bond indices has been calculated for two coordinated acetylide ions coming together. The results are presented in Tables III and IV. Here P is the Wiberg index and Q is the overlap population. It is seen that in comparison with a free acetylide ion, in the coordinated HC≡C⁻ the population of the sp-hybrid orbital decreases, *i.e.*, some delocalization of the negative anion charge occurs. The C≡C bond index slightly decreases too. The orbital of the unpaired electron, consisting mainly of the $3d_{z^2}$ metal orbital, contains a small admixture of the sp-hybrid orbital of the second carbon atom. It means that when the coordinated acetylide ions

TABLE IV. Variation of Atomic Charges with the Distance r in the Linear Model of an Intermediate Complex.

r (A)	q_{Cu}	$q_{Cu} + q_L$	q_{C_1}	q_{C_2}
1.5	−0.0717	0.8040	−0.0041	0.0822
2.0	−0.0577	0.8190	0.0211	0.0500
2.5	0.1021	0.9817	0.0231	−0.0895
∞	0.4209	1.2911	−0.0236	−0.2887
§	–	–	−0.1089	−0.7292

[a]Free HC≡C$^-$ ion.

TABLE V. Indices of C_2–C_2' Bond and sp-Hybrid Orbital Population of C_2 Atom Depending on the Level of the Metal Orbital in the Model System for $r(C_2–C_2') = 2$ A.

U_M (eV)	C_2–C_2'		sp-Orbital Population	HC≡C Fragment Charge
	P	Q		
[a]	0.2511	0.2162	1.75	1.0000
−15	0.1405	0.2339	1.75	0.9137
−20	0.3149	0.4625	1.48	0.5419
−25	0.7444	0.7440	1.15	0.1280
[b]	0.9409	0.8378	1.03	0.0000

[a]HC≡C$^-$ $^-$C≡CH system. [b]HC≡C$^\bullet$ $^\bullet$C≡CH system.

approach each other, direct electron transfer can occur between these orbitals, accompanied with the spin density transfer from the metal to C_2, and the charge transfer in the opposite direction (see Table IV). The charge population of the sp-hybrid orbital approaches unity and a covalent bond arises between C_2 and C_2' atoms. At a distance of 2 Å the index P of the C_2–C_2' bond is already 0.8036, while the sp-orbital population is 1.0505. Note that when the coordinated acetylenes come together, the Wiberg index of C≡C and $\mathrm{Cu}-\overset{\mathrm{C}}{\underset{\mathrm{C}}{|||}}$ bonds slightly decreases. The value of the calculated energy barrier, about 7 eV, should not be considered as a quantitative characteristic since both for it and the absolute value of ΔE this method provides grossly overestimated values.

In Table V the Wiberg index of C_2–C_2' bonds and the populations of sp-hybrid orbitals of C_2 (at r = 2 Å) calculated in the model approximation are compared with their values during the interaction of uncoordinated acetylenic radicals and anions. In the model calculation only one d_{z^2} AO of the metal was taken into account, the energy level of its electron U_M being varied. As seen from the Table, when the level U_M gets lower, the charge tranfer from the acetylenic fragment and the sp-hybrid AO to the metal increases accompanied with the corresponding growth of the C_2–C_2' bond index P. Thus, one can formally proceed continuously from anions to radicals at a sufficiently low metal orbital level at which the d_{z^2} orbital is practically completely populated. In other words, the factors affecting lowering of the level of the metal d_{z^2} orbital must favour the synchronous mechanism.

In the case of dimeric model of the intermediate state, it is an angle ϕ that determines the reaction coordinate (Fig. 2b). In the initial state ($\phi = 90°$) HC≡C$^-$ fragments can form a *cis*-configuration when hydrogen atoms are placed at one side of XZ-plane and a *trans*-configuration when they are at different sides. In the former case the conrotation of acetylide fragments results in a bond, while in the latter case the disrotation leads to it. If in the initial state the distance between C and Cu atoms, determined by van der Waals radii of carbon atoms, equals 3.6 Å, both rotations according to our calculations lead to decrease of the total energy. At $\phi = 0°$, we come to the linear intermediate state with r = 2.22 Å, for which P = 0.5318, Q = 0.3587 are sufficiently large and differ slightly from those in the above linear model. Thus, one can assume that the formation of the initial dimeric state is the most responsible stage of the synchronous mechanism.

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