Physical Chemistry

Quantum-chemical studies of catalysts immobilized on silica. The complex $Cu(OSiH_3)_2 \cdot 2H_2O$ as a model of catalytically active polycopperphenylsiloxanes

V. V. Smirnov,[a] E. N. Golubeva,[a] and M. M. Levitskii[b]*

[a]Department of Chemistry, M. V. Lomonosov Moscow State University, Leninskie Gory, 119899 Moscow, Russian Federation. Fax: +7 (095) 932 8846. E-mail: smirnov@kinet.chem.msu.ru
[b]A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 ul. Vavilova, 117813 Moscow, Russian Federation. Fax: +7 (095) 135 5085

The structures of the complexes $CuX_2 \cdot 2L$ (X = OH, $OSiH_3$, or Cl; L = H_2O, NH_3, H_2S, or PH_3) were calculated and their electron affinities were estimated by the MP2//HF/SBK(6-31) method. The $[CuX_2 \cdot 2L]^-$ anions are unstable and decompose to chlorocuprite anions and free ligands. Based on the results of calculations for the complex $Cu(OSiH_3)_2 \cdot 2H_2O$ (the simplest model of the structural unit of polycopperphenylsiloxane) and possible products of its conversions, the catalytic properties of polycopperphenylsiloxanes in the reactions of chloroorganic synthesis are discussed.

Key words: quantum-chemical calculations, copper chloride complexes, electron affinity, polycopperphenylsiloxanes, silica, heterogeneous catalysis.

Silica-immobilized copper-containing polyorganosiloxanes (in particular, polycopperphenylsiloxanes (PCPS)) exhibit catalytic activity in conversions of chlorocarbons (for examples, in metathesis of C—Cl bonds[1] and in allylic isomerization of dichlorobutenes[2]). Redox processes involving copper ions are of importance in these reactions. For example, it is assumed that metathesis involves reduction of the starting Cu^{II} ions to Cu^{I} ions through one-electron transfer from the organic ligand to the metal atom and the reaction of the resulting Cu^{I} complex with carbon tetrachloride to form the trichloromethyl radical accompanied by reoxidation of the copper ion. The trichloromethyl radical is involved in further chain propagation and the formation of final reaction products.

Processes leading to a change in the valence state of copper atoms in PCPS are still not understood. In this connection, it was of interest to perform calculations for species modeling the structural units of PCPS and to estimate the relative efficiency of redox processes involving these species compared to those with the participation of other copper-containing complexes.

Published in *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 9, pp. 1499—1503, September, 2000.,
1066-5285/00/4909-1491 $25.00

Calculation procedure

The geometries of copper complexes were optimized using the SBK effective core potential.[3] The energies of species were refined using the second-order Möller—Plesset perturbation theory (MP2). Apparently, this level of approximation allows one to adequately describe, on the whole, monovalent and divalent copper complexes.

Results and Discussion

A comparison of results of calculations with experimental data presents difficulties because data on the energies of metal—neutral ligand bonds in the gas phase are scarce. To verify the validity of the method, we calculated the hydration energies of the Cu^+ ion in the gas phase (E_{hydr}), for which reliable experimental data on gas-phase processes are documented:[4]

$$Cu^+ + H_2O \longrightarrow Cu(H_2O)^+, \quad (1)$$

$$Cu(H_2O)^+ + H_2O \longrightarrow Cu(H_2O)_2^+. \quad (2)$$

The calculated values are 39.5 and 37.8 kcal mol^{-1} for processes (1) and (2), respectively. The corresponding experimental values are in the ranges of 35—38 and 37—39 kcal mol^{-1}, respectively. The fact that the calculated and experimental values are in close agreement provides evidence that this method is suitable for solution of the problems under consideration.

Researchers face approximately the same problems when calculating the geometric parameters because the quantitative data on the gas phase are also scarce. The experimental Cu—F distance in the well-studied CuF_2 molecule is 1.713 Å.[5] Calculations in the above-mentioned approximation gave a linear structure with a distance of 1.75 Å. The molecule of copper monohydroxide in the gas phase is nonlinear, the Cu—O and O—H distances are 1.78 and 1.03 Å, respectively, and the bond angle is 111°.[6] The corresponding calculated values are 1.83 Å, 0.96 Å, and 116°. In copper nitrate with the square configuration of the central ion, the Cu—O distance is 1.95 Å.[7] The calculation led to a similar geometry with a distance of 1.97 Å. On the whole, it can be stated that the chosen approximations allow one to adequately determine the geometry in a qualitative sense and to achieve a satisfactory quantitative agreement between the calculated and experimental values.

Since the ionization potentials and electron affinities of copper complexes are of fundamental importance in making conclusions in this work, the results obtained in the above-mentioned approximations were compared with the results of calculations using a more extended basis set with additional polarized d-orbitals of heavy atoms (an analog of the STO 6-31G* basis set), the energies being refined with the use of the perturbation theory (the MP2 method). The vertical electron affinity of the $CuCl_2$ molecule and the vertical ionization potential of the equilibrium configuration of the $CuCl_2^-$ ion were calculated. The differences between the values calculated in the two approximations are at most 0.1 (<2%) and 0.2 eV (<4%) in the first and second cases, respectively. Analogous results were obtained for the $Cu(OH)_2$ and $Cu(OH)_2^-$ systems. Therefore, further extension of the basis set is obviously unreasonable.

Choice of a model of PCPS and reaction intermediates. Oligomeric PCPS used[1,2] for the preparation of silica-immobilized catalysts contain interacting fragments in which the metal ions are in a nearly planar-square environment, which is formed by four O atoms covalently bound to Si atoms. The precise internuclear Cu—O distances are lacking. In crystalline PCPS possessing similar properties, these distances are in the range of 1.90—1.95 Å.[8] We chose the complex $Cu(OSiH_3)_2 \cdot 2H_2O$ (**A**) as the simplest model of the Cu^{II} ion in such an environment. In the chosen complex, the Cu atom is surrounded by four O atoms, two of which, like those in PCPS, being covalently bound to the Si atoms. An alternative $Cu(OSiH_3)_4$ model is unsuitable because this complex occurs as a dianion and cannot be considered as a model of the neutral (as a whole) fragment of PCPS.

The efficiency of redox processes of the metal atom depends not only on the nearest environment, but also on a large number of different factors, *viz.*, on the properties of the medium, the temperature, the chemical nature of the reducing agent, *etc.*, which makes calculations of the absolute rates of these processes unfeasible. However, a comparison can be carried out in a series of related compounds and the effect of the nature of the ligand on the properties of the complex can be estimated. In this work, we chose $Cu(OH)_2 \cdot 2H_2O$ (complex **B**) and $CuCl_2 \cdot 2H_2O$ (complex **C**) for comparison with model complex **A**. System **C** is of interest because the chlorine-containing complexes have been used for the preparation of immobilized catalysts in most studies devoted to metathesis and isomerization of chloroolefins.[9,10] In addition, calculations were carried out for the compounds $CuCl_2 \cdot 2NH_3$ (**D**), $CuCl_2 \cdot 2H_2S$ (**E**), and $CuCl_2 \cdot 2PH_3$ (**F**), which are models of complexes with amine, thioester, and phosphine ligands, respectively, exhibiting catalytic activity in conversions of chlorocarbons.[11]

Structures of $CuX_2 \cdot 2L$ complexes. In complexes **A**, **B**, **D**, and **F**, the nearest environment about the central ions is a planar square. The deviations from the ideal square configurations are associated with small differences in the distances from the central ion to the ionic (X) and neutral (L) ligands. Complex **E** is characterized by a slight distortion of the planar structure, *viz.*, one of the Cl ions deviates from the plane passing through the central ion and the three other ligands (the Cl—(Cu—Cl—S) dihedral angle in this complex is −157°, and the corresponding angle in the totally planar form is −180°). Finally, according to the results of calculations, complex **C** has a nonplanar (nearly tetrahedral) structure (the angle between each of the Cu—O′ and Cu—Cl″ bonds and the Cu—O″—Cl plane is 126°).

As shown below, the strength of the metal—neutral ligand bond is of considerable importance in catalysis (bonds between ionic ligands and metal atoms are much stronger, and this dissociation is not considered here). We estimated the average bond energy E_D at one-half of the calculated change in the energy of the system in the following process

$$CuX_2 \cdot 2L \longrightarrow CuX_2 + 2\,L. \qquad (3)$$

The internuclear distances in the complexes and the energies of the bonds with the ligands are given in Table 1.

It can be seen that the strength of the metal—ligand bond in the related complexes changes in the series N > O > P ≥ S depending on the nature of the heteroatom. This result agrees well with the known classification of acids and bases proposed by Pearson.[12] According to this classification, Cu^{II} belongs to rather hard Lewis acids and reacts preferentially with typical hard bases (water and ammonia) and substantially less readily with soft P- and S-containing bases. The replacement of OH^- as an ionic ligand by Cl^- has virtually no effect on the strength of the bond with the molecular ligand (water); however, the introduction of the $OSiH_3^-$ group instead of these ligands substantially destabilizes the bond with water (see Table 1).

Electron affinities of the complexes. The simplest mechanism of activation of C—Cl bonds in polyhaloalkanes with copper complexes assumes reactions of the following type[13]:

$$Cu^{I} + CCl_4 \longrightarrow Cu^{II}Cl + CCl_3^{\cdot}, \qquad (4)$$

where Cu^{I} and $Cu^{II}Cl$ represent mono- and divalent copper compounds involved in the reaction. Regeneration of the active Cu^{I} complex also requires a redox process, *viz.*, a reaction either with the molecule of a reducing agent (in particular, a ligand can serve as such a molecule) or with an organic radical according to the following scheme:

$$CCl_3^{\cdot} + RH \longrightarrow CHCl_3 + R^{\cdot}, \qquad (5)$$

$$R^{\cdot} + Cu^{II}Cl \longrightarrow RCl + Cu^{I}. \qquad (6)$$

Table 1. Internuclear distances (R) and energies of bonds with ligands (E_D) in four-coordinate copper complexes according to the results of calculations by the MP2//HF/SBK (6-31G) method

Complex	X	L	R(Cu—X)	R(Cu—L)	E_D
			Å		/kcal mol^{-1}
A	$OSiH_3$	H_2O	1.850	2.077	15.9
B	OH	H_2O	1.862	2.098	23.4
C	Cl	H_2O	2.277	2.067	23.5
D	Cl	NH_3	2.377	2.082	37.6
E	Cl	H_2S	2.241	2.658	15.8
F	Cl	PH_3	2.280	2.656	18.8

In this case, both the ability of Cu^{II} in PCPS to undergo reduction to Cu^{I} and the activity of the resulting Cu^{I} complex in the redox reaction with polyhaloalkane are of fundamental importance. Clearly, the situation where both reactions readily occur is optimum.

A Cu^{II} complex can be reduced either through one-electron transfer from a particular donor reagent or in the course of a usual thermal reaction with a reducing agent in which the electron density redistribution is accompanied by the geometric rearrangement of the system (the adjustment of the geometry to the redox process). To a first approximation, the vertical electron affinity, which can be determined as the difference between the energies of the initial species and the one-charge negative ion with the identical geometry, can serve as a measure of activity of Cu^{II} in processes of the first type.

The calculated vertical electron affinities (A_v) and the corresponding values for the ligand-free CuX_2 species are given in Table 2. It can be seen that in many cases the electron affinities of the $CuX_2 \cdot 2L$ complexes are substantially lower than those of the corresponding CuX_2 compounds. Therefore, any ligand destabilizes a negative ion in the reduced form. Actually, geometry optimization of the $\{CuX_2 \cdot 2L\}^-$ species resulted in their degradation to form three remote molecules:

$$\{CuX_2 \cdot 2L\}^- \longrightarrow CuX_2^- + 2\,L. \qquad (7)$$

This result agrees with the known experimental fact that negatively charged mononuclear Cu^{I} complexes have linear structures in which the coordination number of the copper atom is generally equal to 2. Reaction (7) is accompanied by (particularly, in the case of complex **C**) the formation of weak hydrogen bonds between the leaving water molecules and the anionic ligands. We ignored this effect, which makes only an insignificant contribution (several kcal mol^{-1}) to the total energy of the process. Moreover, it is unlikely that this effect is manifested in real immobilized catalysts in which the leaving ligand can form stronger hydrogen bonds with the surface hydroxide groups of the carrier.

Table 2. Vertical (A_v) and adiabatic (A_a) electron affinities of the complexes $CuX_2 \cdot 2L$ and CuX_2 and the vertical ionization potentials (I_v) of the CuX_2^- ions

Complex	A_v	A_a	I_v
		eV	
A	1.34	—	—
B	0.20	—	—
C	2.56	—	—
D	1.72	—	—
E	3.56	—	—
F	3.02	—	—
$Cu(OSiH_3)_2$	3.62	3.70	4.08
$Cu(OH)_2$	3.15	3.42	3.54
$CuCl_2$	5.12	5.22	5.40

Therefore, thermal reduction of Cu^{II} complexes can occur as a two-step process involving elimination of neutral ligands, which destabilize the anionic form, followed by reduction of strong oxidizers CuX_2:

$$CuX_2 \cdot 2L \longrightarrow CuX_2 + 2\,L,$$

$$CuX_2 + e \longrightarrow CuX_2^-$$

As mentioned above, it is possible that both processes occur simultaneously. However, it seems reasonable to expect that the conclusions reached on the assumption that this process occurs according to a two-step mechanism are also true for the case under consideration.

According to the data in Table 2, all complexes under study, except for complex **B**, possess substantial electron affinities and can be readily reduced. In these cases, adjustment of the geometry is not needed. For complex **B**, a two-step mechanism involving intermediate elimination of the ligands is more probable. Complex **A**, which is of interest to us as a model of PCPS, is an intermediate between **B** and the remaining compounds because its electron affinity is rather high and yet is lower than those of other complexes. From this viewpoint, an important point is that the neutral ligands in this complex are rather weakly bound to the metal atom (see Table 1). Therefore, both mechanisms (the two-step mechanism of dissociation—reduction and the mechanism of one-electron transfer) seem to be possible.

The rate of generation of radicals in the reactions of CCl_4 with the Cu^I complexes depends on the reducing ability of the latter. The formation of the radicals is most likely to be preceded by one-electron transfer from the metal atom to CCl_4. The ionization potential of the metal complex can serve as a measure of the efficiency of the latter process. The instability of four- and even three-coordinate negatively charged copper(I) compounds leads to the fact that reoxidation of the metal atom with polyhaloalkanes should occur with the participation of CuX_2^- anions and, hence, their ionization potentials are of importance for estimating the activity of the system. It can be seen in Table 2 that the vertical ionization potential of the anion, which was prepared from the complex chosen by us as a model of PCPS, is substantially lower than that of $CuCl_2$ and is comparable with that of the $Cu(OH)_2^-$ anion.

Therefore, we can suggest that the copper atoms in PCPS are reduced somewhat more difficultly than those in the corresponding dissolved chloride complexes, but very readily undergo reoxidation. In this case, the reduction of copper should be accompanied by destruction of the regular structure of PCPS, which is built of planar-square CuO_4 units linked in a common system,[8] and by the formation of Cu^I ions (more precisely, by the formation of negatively charged fragments of PCPS containing monovalent copper atoms) with the coordination number of 2. It can also be suggested that the specific catalytic activities of PCPS are close to or somewhat lower than those of catalysts based on chloride complexes. Within the framework of the concepts under consideration, the rate-determining stage in catalysis on PCPS involves reduction (one- or, more likely, two-step) of Cu^{II}. Therefore, in the course of catalytic processes, the major portion of copper in PCPS, unlike catalysts based on chloride complexes, should exist in the oxidation state +2. Finally, one would expect that the synthesis of PCPS, in which the formation of CuO_4 aggregates is hindered (for example, by introducing bulky substituents into the initial siloxane derivative), will afford a catalyst which is much superior in activity per metal ion to the highly ordered systems used previously. All these suggestions can be experimentally verified. Currently, we are performing these studies. Preliminary data demonstrated that the above-mentioned predictions are, on the whole, justified.

In conclusion, note that the results obtained in this work make it possible to explain also some peculiarities of the behavior of catalysts based on complexes of copper chloride with amides applied onto silochrom. The experimental data[9,10] indicate that the activity of these catalysts decreases in operation, the major portion or virtually all organic ligands being lost and Cu—O bonds being formed. One could suggest that the Cu atoms surrounded by O atoms are inactive in reactions with polyhaloalkanes. However, the above-considered results of calculations demonstrated that the activity of these complexes should not be substantially lower than that of chloride complexes. Consequently, the loss of the organic donor ligand, which acts as a reducing agent, in the course of side reactions is the only reason for deactivation. Note that deactivation of PCPS containing an electron-donating fragment (an aromatic substituent) is not observed.

To verify this hypothesis, we carried out a model experiment using a procedure analogous to that employed previously.[9,10] Thus the catalytic activities of two chloride complexes of copper with dimethylformamide and caprolactam, which were supported on silica gel, were measured (1 and 0.85, where 1 is the initial activity of the DMF-containing catalyst) after which these complexes were heated at 180 °C for 24 h in the presence of a mixture of CCl_4 with *n*-decane taken in a molar ratio of 4 : 1. Then the catalysts were washed and the catalytic activities were measured once again. The activities appeared to be very low (0.12 and 0.22, respectively). However, when 2 mol.% of the corresponding amide was introduced into the reaction mixtures, the initial activities were restored (1.07 and 0.83, respectively). This experiment demonstrated that the above-considered description of the process is, on the whole, adequate, and the results of quantum-chemical calculations can be used for the prediction of the behavior of the system.

This work was financially supported by the Russian Foundation for Basic Research (Project Nos. 00-03-32154 and 00-03-32211).

References

1. V. V. Smirnov, E. N. Golubeva, and O. V. Zagorskaya, *Kinet. Katal.*, 2000, **41**, 439 [*Kinet. Catal.*, 2000, **41**, No. 2 (Engl. Transl.)].
2. V. V. Smirnov, M. M. Levitskii, S. M. Nevskaya, and E. N. Golubeva, *Kinet. Katal.*, 1999, **40**, 86 [*Kinet. Catal.*, 1999, **40** (Engl. Transl.)].
3. W. J. Stevens, H. Basch, and M. J. Krauss, *J. Chem. Phys.*, 1984, **81**, 6026.
4. T. F. Magnera, D. E. David, D. Stulik, R. G. Orth, H. T. Jonkman, and J. Michl, *J. Am. Chem. Soc.*, 1989, **81**, 5036.
5. N. Yu. Subbotina, G. V. Girichev, and A. V. Ostrolinov, *Zh. Strukt. Khim.*, 1989, **30**, 42 [*J. Struct. Chem. USSR*, 1989, **30** (Engl. Transl.)].
6. C. N. Jarman, W. T. M. Fernando, and P. F. Bernath, *J. Mol. Spectr.*, 1991, **145**, 151.
7. S. Shibata and K. Iijima, *J. Mol. Struct.*, 1984, **117**, 45.
8. E. Rentscher, D. Gatteschi, A. Corina, A. C. Fabretti, A.-L. Barra, O. I. Shchegolikhina, and A. A. Zhdanov, *Inorg. Chem.*, 1996, **35**, 4427.
9. E. N. Golubeva, S. M. Nevskaya, V. V. Vorontsov, and Ya. M. Abdrashitov, *Izv. Akad. Nauk, Ser. Khim.*, 1997, 1835 [*Russ. Chem. Bull.*, 1997, **46**, 1741 (Engl. Transl.)].
10. E. N. Golubeva, A. I. Kokorin, V. V. Smirnov, P. I. Vorontsov, and D. A. Koval'skii, *Kinet. Katal.*, 1998, **39**, 908 [*Kinet. Catal.*, 1998, **39** (Engl. Transl.)].
11. V. V. Smirnov, T. N. Rostovshchikova, and E. N. Golubeva, *Ros. Khim. Zh. (Zh. Ros. Khim. Obshch. im. D. I. Mendeleeva)*, 1998, **42**, 49 [*Mendeleev Chem. J.*, 1998, **42** (Engl. Transl.)].
12. R. J. Pearson, *Usp. Khim.*, 1971, **40**, 1259 [*Russ. Chem. Rev.*, 1971, **40** (Engl. Transl.)].
13. M. Assher and D. Vofsi, *J. Chem. Soc., B*, 1968, 947.

Received July 27, 1999;
in revised form March 9, 2000