Quantum-chemical investigation of Cu-containing catalysts for C−Cl bond metathesis

Vladimir V. Smirnov [*], Elena N. Golubeva

*Moscow Lomonosov State University, Leninskie Gory, Moscow 119899, Russia*

Abstract

Ab initio calculations modelling catalysts of C−Cl bond metathesis were carried out. The complicated catalytic system consisted of three different groups of components — amides, copper complexes in different oxidation states and inorganic support. The results of calculations, in good agreement with experimental data, explain the way of fixing the active catalyst on silica surface, describe geometrical parameters and redox properties of copper complexes with donor ligands, verify some key stages of the proposed mechanism of metathesis. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Catalysis; Copper complexes; C−Cl bond metathesis; Ab initio calculations; Redox processes

1. Introduction

The reaction of C−Cl bond metathesis is Cl–H exchange between Cl-reach compounds and hydrocarbons.

$$RCl_n + R'H_m \rightarrow RCl_{n-1}H + R'H_{m-1}Cl \qquad (1)$$
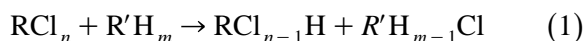
The reaction is simple on paper, but very difficult in practical realization even in lab conditions. This way of proficient use of carbon tetrachloride, polychlorobenzenes and other wastes in functionalization of hydrocarbons is obviously very attractive, and during the last 20 years scientists made attempts to put it into practice. However, only solitary papers and patents were published [1–5], and none of the methods is sufficient both in productivity and selectivity.

Recently, we worked out the systems for catalytic initiation of metathesis which substantially surpass those known earlier [6]. They combine good activity, high selectivity and accessibility. The catalysts are complexes of copper chlorides with amides such as dmf or caprolactame immobilized in pores of some inorganic supports, e.g. silica. It was found that the adsorptive layer of dmf should exist on the surface of the active catalyst — removing of dmf resulted in a significant loss of the activity [7]. Dmf facilitates the immobilization of copper complexes — the lack of copper is negligible even in conditions of liquid-phase reaction [6]. We gave evidence that there are interactions of dmf with silanol groups of silica which are responsible for the fixation [7]. Dmf forms very stable lamina on the surface, and copper ions due to forming strong complexes with dmf preferably distributed in it. Furthermore, it is in a dmf media in which active cupric complexes

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[*] Corresponding author.
E-mail address: eng@excite.chem.msu.su (V.V. Smirnov).

form. Four types of labile mononuclear neutral and ionic complexes of Cu(II) with chloride anions and (or) dmf molecules are formed in pores of the catalyst or in dmf solution [8]. They are at least by order of magnitude more active than polynuclear complexes of cupric chloride with dmf in low-polar media such as chlorobenzene, polycristalline cupric chloride on the surface of silica or catalysts obtained by the way of ionic exchange. And finally, dmf plays very important role in the catalyst evolution.
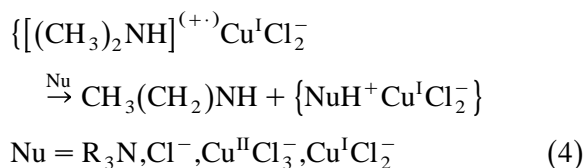
Let us consider the third factor in detail. We observed induction periods on kinetic curves of metathesis. In parallel the chemical composition of the catalyst changed — dmf partially decomposed into diethylamine and CO

$$(CH_3)_2NCHO \xrightarrow{Cu^{2+}} (CH_3)_2NH + CO \qquad (2)$$
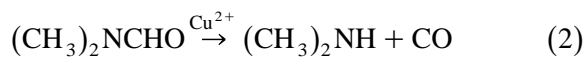
It is well known that amines could easily reduce Cu(II) to Cu(I) [9,10]

$$(CH_3)_2NH + Cu^{II}Cl_2$$
$$\rightarrow \left\{ [(CH_3)_2NH]^{(+\cdot)} Cu^I Cl_2^- \right\} \qquad (3)$$
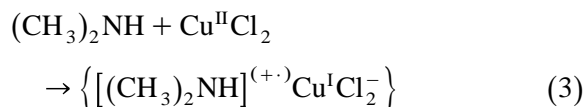
We proposed that different nucleofils could promote transformation of the radical-cation to radical

$$\{[(CH_3)_2NH]^{(+\cdot)} Cu^I Cl_2^-$$
$$\xrightarrow{Nu} CH_3(CH_2)NH + \{NuH^+ Cu^I Cl_2^-\}$$
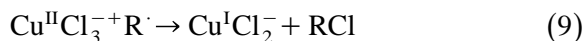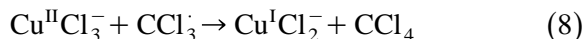$$Nu = R_3N, Cl^-, Cu^{II}Cl_3^-, Cu^I Cl_2^- \qquad (4)$$

The formed cuprous complexes may transfer electron to carbon tetrachloride followed by formation of trichloromethyl radicals and Cu(II) complexes:

$$Cu^I Cl_2^- + CCl_4 \rightarrow \{Cu(II)Cl_2 \ldots CCl_4^{(-\cdot)}\}$$
$$\rightarrow Cu(II)Cl_3^- + CCl_3^{\cdot} \qquad (5)$$
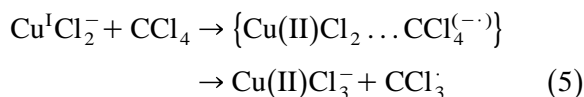
Trichloromethyl radicals take part in chain propagation:

$$CCl_3^{\cdot} + RH \rightarrow CHCl_3 + R^{\cdot} \qquad (6)$$

$$R^{\cdot} + CCl_4 \rightarrow RCl + CCl_3^{\cdot} \qquad (7)$$
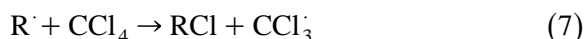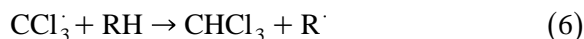
We suppose that different radicals could reduce Cu(II) to Cu(I), recycling the initiator and completing the catalytic cycle:

$$Cu^{II}Cl_3^- + CCl_3^{\cdot} \rightarrow Cu^I Cl_2^- + CCl_4 \qquad (8)$$

$$Cu^{II}Cl_3^- + R^{\cdot} \rightarrow Cu^I Cl_2^- + RCl \qquad (9)$$

Some of stages in the scheme are well investigated, some of them are proposed and need theoretic or experimental verification, and we can now formulate some problems, which are difficult to solve only experimentally. How are the active catalyst attach to the silica surface? How could redox reactions with partition of copper ions result in generation of organic radicals? Is the mechanism of metathesis based on alternate reduction–oxidation of copper ions realistic? What is the reason (besides of trivial carbonization) of changes in catalytic activity during its prolonged work?

2. Calculation details

We had to simulate several quite different groups of components — organic compounds, copper complexes in different oxidation states and, finally, inorganic support. A few approaches are developed for description of each of the group. The most trivial kind of objects is organic compounds. Modern semi-empirical and all the more ab initio calculations simulate them correctly. The methods of copper complexes calculations are developed worse — in many approximations even a parameterization or basis sets for copper atom are absent. In some methods, which were parameterized (e.g. ZINDO/1), some significant discrepancies with experiment are observed. For example, the value of electrostatic interactions in Cu(I) complexes is overrated resulting in giving too high values of bond strength of the central ion with water, alcohols and other hard bases. Some parameters of the support (e.g. bond lengths Si—O) are also described absolutely incorrectly. Ab initio full electron calculations with standard basis sets,

Table 1
Experimental and calculated energies (H.E.) of Cu^+-ion gas-phase hydration (in kcal/mol)

Reaction	H.E., exp.	H.E., calc.
$Cu^+ + H_2O \rightarrow Cu(H_2O)^+$	35–38	39.5
$Cu(H_2O)^+ + H_2O \rightarrow Cu(H_2O)_2^+$	37–39	37.8

e.g. STO 6–31* are suitable for cuprous complexes, but in case of Cu(II) the self-consistence is not reached even for very simple structures. Most of these problems are kept off in approximations using effective core potential. This approach is suitable for calculation of complexes of transition metals [11]. We used the potential developed by Stewens et al. [12] combined with descriptions of valence electrons as in the basis STO 6–31G. Energies were corrected on the level second order Möller–Plesset perturbation theory. Comparison of some calculated and experimental values for Cu complexes shows the adequacy of the approach (Table 1). It seemed that the applicability of it to the third part of the catalyst — surface groups of silica and their hydrogen — bonded complexes was not checked. It forced us to investigate this problem more carefully. We used silicic acid and its water complex $HO-Si(=O)-OH \ldots OH_2$ (complex C1) as the simplest model. The key

values such as internuclear distances of complex and its stabilization energy are almost as accurate as obtained in full-electron calculation on MP2/6–31** level (Table 2).

The problem of a correct choice of the model of silica surface is investigated during many years, but no common conclusion was done about the appropriate size of the silicon–oxygen cluster and the nature of terminal groups. Some authors use the simplest cluster $Si(OH)_4$ as a model of isolated silanol groups [13], but for precise description big clusters, based on four to six or more bonded silicon–oxygen tetrahedrons with silicon-containing terminal groups should be used [14]. We chose a middle-sized cluster $(H_3SiO)_3SiOH$ containing four silicon atoms as in most recent papers concerned with calculations of silica and zeolites [15].

3. Results and discussion

The first question to investigate was the nature of fixing of the active heterogeneous catalyst containing the excess of dmf along with copper complexes in silica pores. Thus, we had to compare the energies of interactions of silanol groups with amides and cupric complexes. The

Table 2
Interatomic distances in complex C1 (R,Å) and its stabilization energy in comparison with isolated molecules (E_s, kcal/mol)

Calculation level	R(Si=O)	R_1(Si−O)[a]	R_2(Si−O)[b]	R(O−H)[c]	R(H....O)	E_s
HF/6–31G	1.569	1.639	1.657	0.944	1.680	13.2
HF/6–31G[a]	1.494	1.607	1.618	0.949	1.866	10.0
HF/6–31G[b]	1.494	1.604	1.615	0.944	1.875	10.0
MP2/6–31G	1.603	1.692	1.707	0.973	1.699	16.3
MP2/6–31G[a]	1.534	1.635	1.647	0.987	1.770	13.8
MP2/6–31G[b]	**1.535**	**1.638**	**1.649**	**0.965**	**1.767**	**13.2**
HF/SBK(6–31G)	1.561	1.632	1.647	0.944	1.647	12.5
MP2//HF/SBK(6–31G)	1.561	1.632	1.647	0.944	1.647	13.6
HF/SBK(6–31G[a])	1.494	1.603	1.613	0.960	1.874	8.2
HF/SBK(6–31G[b])	1.495	1.600	1.611	0.956	1.844	8.2
MP2/SBK(6–31G)	1.603	1.692	1.707	0.973	1.676	15.0
MP2/SBK(6–31G[a])	1.534	1.637	1.650	0.987	1.755	11.9
MP2/SBK(6–31G[b])	1.534	1.635	1.647	0.978	1.721	11.3

[a] Si−O distance in SiOH group bound with water molecule.
[b] Si−O distance in free SiOH group.
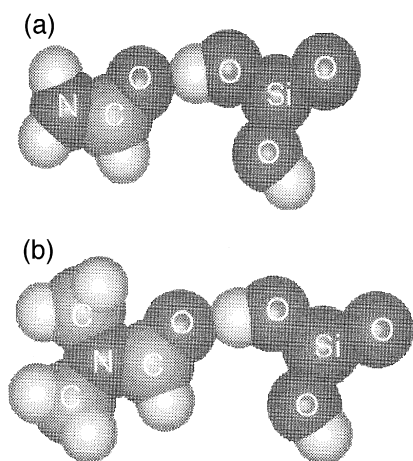[c] O−H distance in OH group bound with water molecule.

(a)

(b)

Fig. 1. The optimized geometries of silicic acid complexes with fa C2 (a) and dmf C3 (b).

Fig. 2. The optimized geometry of the model of adsorption complex dmf–silica C4.

formamide (fa) was taken as a simplest amide. The systems silicic acid–fa (C2) and silicic acid–dmf (C3) are compared in Fig. 1. It is seen that the fragment C=O...HO−Si in both structures is close to planar as in the complex with water. The lengths of intermolecular bonds do not strongly differ (Table 3), and the stabilization energy arises a little in dmf complex (15.0 kcal/mol in comparison with 13.4 kcal/mol for fa complex). These values are usual for rather strong complexes with hydrogen bond.

The complex modeling the adsorption of fa on silica surface (C4) is given in Fig. 2. Once again the fragment C=O...HO−Si is planar,

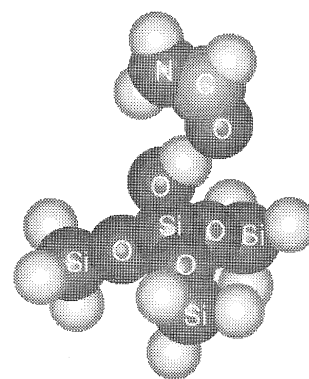the stabilization energy is 13.6 kcal/mol. The main distances are:

$R(C-N)$ in amide	1.357 Å
$R(C-H)$ in amide	1.101 Å
$R(C-O)$ in amide	1.246 Å
$R(O...H)$ intermolecular	1.864 Å
$R(H-O)$ in $HOSi(OSiH_3)_3$	0.975 Å
$R(O-Si)$ in $HOSi(OSiH_3)_3$	1.680 Å

The angles are:

< NCH in amide	115.4°	?HCO in amide	120.6°
< CO...H	138.6°	?O...H−O	176.6°

Thus, amides could form a stable adsorptive layer on silica due to forming rather strong hydrogen bonds with silanol groups.

Table 3
Interatomic distances (R,Å) in complexes of amides with silicic acid

Amide	Calculation level	$R(Si-O)$[a]	$R(O-H)$[b]	$R(H...O)$	$R(C=O)$
dmf	HF/6–31G	1.613	0.967	1.688	1.235
fa	HF/6–31G	1.609	0.963	1.699	1.228
dmf	HF/SBK(6–31G)	1.617	0.969	1.657	1.249
fa	HF/SBK(6–31G)	1.610	0.967	1.668	1.246
dmf	MP2//HF/SBK(6–31G)	1.617	0.969	1.657	1.249
fa	MP2//HF/SBK(6–31G)	1.610	0.967	1.668	1.245

[a] Si−O distance for OH group bonded with amide molecule.
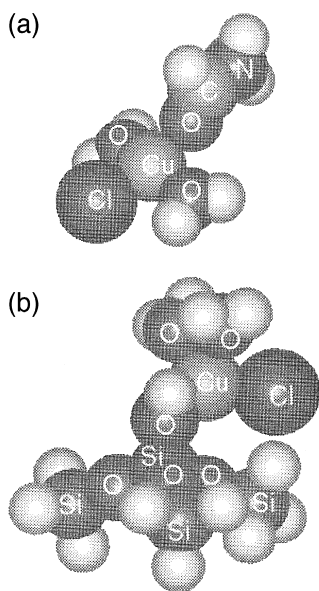[b] O−H distance in OH group, bonded with amide molecule.

(a)

(b)

Fig. 3. The optimized geometries of cupric complexes with fa C5 (a) and silica cluster C6 (b).

The next question was to study the competition between amides and isolated surface OH-groups in coordination sphere of the cupric ion. As a model of amide complex we took $CuCl(fa)(H_2O)_2^+$ (C5) (see Fig. 3a). The model complex has distorted square coplanar configuration in consistency with experimental data for Cu(II)–water systems. The main interatomic distances are:

$R(Cu-Cl)$ 2.245 Å $R(Cu\ldots O=C)$ 1.957 Å
$R(Cu\ldots OH_2)$ 2.018 Å $R(C=O)-$ 1.264 Å

The energy of fa removal is 49.7 kcal/mol and should be about 8–10 kcal/mol higher for dmf (58–60 kcal/mol).

The model of the complex with surface groups (C6) is given in Fig. 3b. The structure of this complex is similar to those described earlier. The internuclear distances are: $R(Cu-Cl) = 2.268$ Å, $R(Cu\ldots OH_2) = 2.030$ Å, $R(Cu\ldots O-(H)-Si(OSiH_3)_3) = 2.036$ Å. The energy of the cluster removal is 62 kcal/mol. Thus, the bonding energies of cupric ions with dmf and surface hydroxyl are of the same magnitude. The ratio

between them in silica pores should depend on the dmf content. When dmf dominates, it should form complexes with the surface group and cupric ions, and we do see it in experiment, but in vacuum-processed and not containing dmf samples we detect interactions of cupric complexes with surface groups.

Redox reactions of copper ions could be responsible for initiation of organic radicals in presence of copper compounds. That is why they may be very important in catalysis of initiation of many reactions including metathesis. However, accurate experimental values of ionization potentials or electron affinities of copper complexes in non-aqueous low-polar media and all the more of adsorbed particles is difficult to obtain experimentally. That is why quantum-chemical investigation could be the most essential in this case.

The first stage of the suggested mechanism is the reduction of cupric ion. It is generally known that coordination environment influence it. We chose complexes of cupric chloride with two molecules of the simplest donors — water, ammonia, hydrogen sulfide and phosphine as models. The main parameters of these complexes are represented in Table 4. Most of complexes have square or slightly distorted square configuration in agreement with multiple experimental data for Cu-complexes. The evaluated energies of metal-ligand bonds are in good agreement with well-known Pirson classification: relatively hard acid — cupric ion — is

Table 4
The main parameters of CuX_2L_2 complexes

X	L	$R(Cu-X)$, Å	$R(Cu-L)$, Å	E_D, (kcal/mol)[a]	A_v, (eV)[b]
Cl	H_2O	2.277	2.067	23.5	2.56
Cl	NH_3	2.377	2.082	37.6	1.72
Cl	H_2S	2.241	2.658	15.8	3.56
Cl	PH_3	2.280	2.656	18.8	3.02
OH	H_2O	1.862	2.098	23.4	0.2
$OSiH_3$	H_2O	1.850	2.077	15.9	1.34

[a] The energy of the ligand (L) removal, calculated as one half of the difference between CuX_2L_2 and $(CuX_2 + 2L)$ energies.
[b] Vertical electron affinities of CuX_2L_2.

stronger bonded with two most hard bases — ammonia and water.

Electron affinities as criteria for easiness of reduction of copper ions were calculated as a difference between energies of an initial particle and a singly charged negative ion of the same structure. It is obvious that rather high electron affinities of the complexes indicate the tendency of these complexes to reduce. Actually, it is known that cupric complexes with a variety of donor ligands, especially with low ionization potentials (phosphines, sulfides, amines) undergo spontaneous reduction to Cu(I) [16].

The geometry optimization of the negative ions with initial coordination number 4 gives three isolated particles. The result is perfectly consistent with experimental data — singly charged negative cuprous ions are linear and Cu coordination number is 2 [16].

The same calculations of electron affinities of cupric hydroxide complex with water give much lower value. It illustrates another experimental fact — different complexes of cupric hydroxide are low active in activation or catalysis of chlorocarbons reactions as compared to cupric chloride. One more structure presented in the picture is the simplest model of cupric ion, chemically bonded with silica surface. Its electron affinity has interstitial value, and we could predict their appreciable catalytic activity.

The suggested mechanism assumes an alternate changes of copper oxidation states. An oxidation of cuprous ions occurs in the reaction with one of substrates — CCl_4. It is this step that initiates radical chain process. Now an opposite property of a complex — an ionization potential (I_v) of stable Cu(I) derivatives CuX_2^- is decisive. Calculated I_v values are 5.41 eV (X = Cl), 4.08 eV (X = OCH_3), 3.54 eV (X = OH). The rather low values confirm suggestions about possibility of electron transfer from cuprous complexes to CCl_4. Hydroxocomplexes of Cu(I) are less stable, but remembering of high energies for their formation we may conclude that it is improbable to use them as catalysts. Calculation data present an interstitial

place of complexes with Cu−O−Si bond. The main problem here — to supply the system with a donor of electrons. And the experiment did show that addition of dmf to worked-out catalyst promotes a new increase of the activity.

Thus, we could choose an adequate approach to describe particles and elementary steps taking place or modeling some stages of new and important reaction — metathesis of C−Cl bond. In agreement with experiment this method explains the way of fixing the active catalyst on silica surface; describes geometrical parameters and redox properties of copper complexes with donor ligands; verifies some key stages of the proposed mechanism of metathesis.

The good consistence of theoretical and experimental results allows us to hope that the calculation approach might be used for prediction of catalytic activity of different copper complexes in catalysis of metathesis of the C−Cl-bond.

Acknowledgements

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