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Transition Metals Complexation-Polarizing/Depolarizing Theory (TMCPDT)

Stefko Borisov Iliev
Village of German, P.C. 1186, 9, Stariat pat St., Sofia, Bulgaria
(38stiliev12@gmail.com)

Abstract- The needs of the Atom Transfer Radical Polymerization (ATRP) method conceived in 1995 have markedly raised the interest in complex compounds of transition metals. Even though these metals are closely related to catalytic chemistry and chemistry of complex compounds, the matters relating to the functional activity of their organic complexes have not yet been fully clarified. Recently, the interest in this field has grown immensely not only because the conventional mechanism (CFM) of ATRP is not a sufficiently convincing theoretical basis, but mainly because of the increased scholarly interest in the complexes of transition metal halogen derivatives.

Literature sources clearly show that the creators of the ATRP method [5,6] have focused their efforts mainly on developing controlled radical polymerization (CRP), while the issues related to transition metal halogen derivatives complexation and the properties of their organic complexes have been broadly considered as a function of the ligand structure and properties [5]. This fact has provided a free theoretical space and an opportunity to develop the TMCPDT.

Keywords- *DMP, TMCPDT, PDFM, EMCC, SFED, IMERS*

I. INTRODUCTION

The main task of this paper is to distinguish TMCPDT from the essence of ATRP, as defined, the analysis of which has given birth to this theory. It also aims, as much as possible, to present it in pure form, as a tool used to explain the complexation of the halogen derivatives (Cl, Br) of transition metals. This was motivated by the obvious identity between PDFM (Polarizing/Depolarizing Functional Mechanism) of ATRP and TMCPDT [1,2], as frequently noted so far. Developed mainly for the copper atom as an ATRP promoter, PDFM unequivocally proved to be applicable in explaining the complexation of all transition metal halogen derivatives used as ATRP promoters. This fact has made it objectively necessary to systemize the information available in this regard and to present it as a single physico-chemical theory of transition metal halogen derivatives complexation, as TMCPDT actually is.

II. MAIN TASK AND CORE THEORETICAL OBJECTIVES OF THIS PAPER

The main task of this paper, as stated in its beginning, is to elaborate three core theoretical objectives:

1. Formation of an active transition metal complex
2. Functional activity of an active transition metal complex
3. Destruction of an active transition metal complex

TMCPDT is presented as a sequence of functionally related physical laws that form the basis for theoretical justification of the proposed theory and for solving the set tasks and objectives.

III. FORMATION OF AN ACTIVE TRANSITION METAL COMPLEX

A. Transition metals

A main feature of these metals is the fact that they are chemical elements with variable valency. This is the result of the low value of energy needed for transition between the outermost and the last but one electronic layer. Due to the presence of semi-occupied electronic orbitals and non-compensated spin electrons, respectively, they are paramagnetic, their compounds are colored and possess a markedly catalytic action both in a free and bonded state [3,4]. They are capable of complexation in all possible valence states. This fact lies in the basis of their efficient use as ATRP promoters. There are numerous data described in literature sources, for instance, references [5-16], etc., for the carrying out of ATRP processes with nearly all transition metals from the side groups of the periodic system (I, IV, VI, VII, VIII), as quoted in [17,18]. A general conclusion was drawn based on the analysis of these data.

When mixing the source components in a reaction medium, excited organic complexes of transition metal halogenides are obtained *in-situ*. In a natural way, these complexes form a standalone, specific group of soluble metal-organic catalysts with high catalytic action, at moderate temperatures.

Within the meaning of the drawn conclusion and from a historical perspective, copper is the classic representative of that catalytic group, mainly because of its easily accessible compounds in low valence states, which makes it highly informative for the theory and technological for the practice of ATRP. This is due to the low level of energy needed for d/s transitions between the outermost and the last but one electronic layers [4], facilitating the giving away of a second valence electron, oxidation to second positive valence ($Cu^{I} \rightarrow Cu^{II}$), and helps form complexes in the two valence states – excited monovalent copper complex (C-x^{I}) and ATRP-inactive bivalent copper complex (C-x^{II}). This is why, out of purely practical considerations, the discussion of the main elements of TMCPDT is mostly related to copper atom.

B. Formation of an active transition metal complex

1) Double molecular polarization of an active complex

The theoretical bases of TMCPDT are the product of the elaboration of a previously accepted working hypothesis – spontaneous occurrence of a physical effect of double molecular polarization (DMP) of the active monovalent copper complex C-x^{I} [1,2]. This hypothesis was adopted as the result of realizing the fact that it is not the ligand (L) and its properties [5] that play the main role in the transition metal complexation, but the strongly negative electric nature of the mobile halogen atom (X) of alkyl halogenide. This property of its X atom allows it, during complexation, to take the place of a central (complex forming) atom, which is a key factor for the occurrence of the DMP effect on the excited complex molecule.

According to the DMP effect, when mixing an initiator (In – alkyl halogenide with a mobile halogen atom), a catalyst (Cat – a transition metal halogenide), a ligand (Lig – mainly nitrogen-containing organic compounds) and a monomer (M – vinyl, acrylic and metacrylic monomers) in a single synthetic reaction, a natively excited metal-organic complex is formed (Fig. 1). The complex is made of electrostatically polarized (ESP) and electrochemically polarized (ECP) molecular fragments R- and -Cu^{I}L. It is a transient excited molecule whose transformation runs in two stages – multi-stage electrostatic depolarization (ESD) and single-stage electrochemical depolarization (ECD).

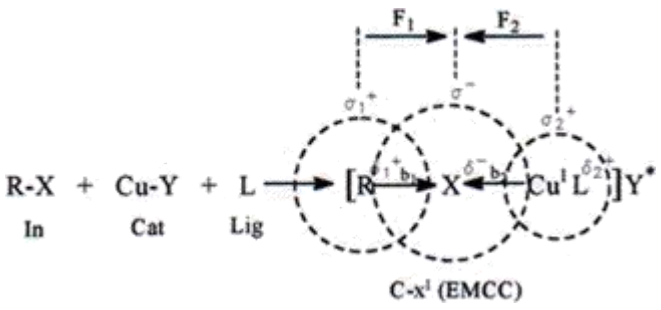

Figure 1. Formation of an active transition metal complex

2) Partial charge transfer

According to PDFM of ATRP [1,2], in complexation, the negative electric charge of the X atom is manifested via the effect of partial charge transfer (CT) between the initiator (R-Cl) and the catalyst (Cu^{I}L). As a result of this effect, an active, excited (E,*) metal-organic complex (C) with bridge-like (μ) structure and coordination number 2 is obtained [19].

According to the Ligand Field Theory, at the formation of complex compounds of transition metals, the inner coordination sphere formation {bonding the molecular orbital (MO)} of the complex is the result of overlapping between the d-orbital of the Cu atom and the p-orbital of the ligand L. Due to the high electronegativity of the X atom, conditions are created to add to the exchange interaction between the electrons of the d- and p-orbitals of the Cu atom and L the exchange interaction with the electrons of the filled-in outer electronic layer of the X atom. At the overlapping of orbitals, a generalized connecting MO of the Cu atom complex is obtained. Its inner coordination sphere, through the X atom, comprises the molecules of both the initiator and the catalyst. Under the influence of the X atom, MO is polarized by a bilateral induction effect (-I), and hence the valence electrons of the molecular fragments R- and -Cu+L are delocalized in the direction of the X atom ($R^{\delta+} \rightarrow X^{\delta-} \leftarrow Cu^{\delta+}$) (Fig. 1). The present covalent bond is polarized to a semipolar bond $R^{\delta+} \rightarrow X^{\delta-}$ (b_1), while between the X atom and the -Cu+L fragment, due to CT, a new semipolar bond $X^{\delta-} \leftarrow Cu^{\delta+}$ (b_2) is formed. By means of b_2, the X atom remains bonded with the Cu atom, but owing to the presence of b_1, the additional oxidation of the Cu atom is hindered.

IV. ELECTROSTATIC POLARIZATION OF AN ACTIVE TRANSITION METAL COMPLEX

By means of the semipolar bonds b_1 and b_2 (Fig. 1), two partial electric charges concentrate on the X atom. Its electron affinity satiates, and it is loaded with a generalized negative electric charge (δ-) transforming into a central atom (-$X^{\delta-}$-) of one excited monovalent copper complex (EMCC) (Fig. 1, the square brackets), with coordination number 2. Because of the different origin of bonds b_1 and b_2, the charge δ^{-} should be considered as being composed of two components of different size (δ_1^{-} and δ_2^{-}), i.e. $\delta^{-} = \delta_1^{-} + \delta_2^{-}$, where ($\delta_1^{-} > \delta_2^{-}$). This is why, upon formation of these bonds, short-term correlation discrepancies occur between their energies and lengths. They condition the temporary existence of a certain amount of non-equilibrium potential energy of the excited state (E_p*), asymmetrically distributed between the molecular fragments R- and -Cu^{+}L of EMCC; therefore, the physical phenomenon of temporary electrostatic polarization (ESP) of the complex molecule occurs. This is due to the fact that (E_p^{*}) is proportional (≡) to a certain asymmetrical (non-equilibrium) electric charge (δ*) on the R- fragment and its corresponding asymmetrical (non-equilibrium) electric potential (φ*), i.e., $Ep^* \equiv \delta^* \equiv \varphi^*$.

The spontaneous tendency towards electrostatic depolarization (ESD) of EMCC, when, at the end of its life cycle, the Ep* complex tends to accept values that are equivalent to the stationary state of the potential energy (E_p) (where $\delta^* = 0$ and $\varphi^* = 0$), leads to a proportional reduction of the inner energy ($-\Delta U$) of the complex ($E_p^* - E_p \equiv -\Delta U$), which is the source of the EMCC functional activity in the conditions of ESP.

A. Structural stability of an active transition metal complex

Because of the bilateral –I effect and the dislocation of valence electrons, the R- and -Cu^+L fragments are loaded with positive electric charges δ_1^+ and δ_2^+, which are reciprocal to δ_1^- and δ_2^- (Fig. 1). In an absolute value, the sum of these charges ($\delta_1^+ + \delta_2^+ = \delta^+$) is equal to the generalized negative electric charge δ^- ($\delta^+ = \delta^-$), i.e., $\delta_1^- = \delta_1^+$ and $\delta_2^- = \delta_2^+$, where $\delta_1^+ > \delta_2^+$. The δ_1^+ and δ_2^+ charges are arranged opposite to the δ_1^- and δ_2^- charges, which gives rise to two Coulomb attraction forces, temporarily compensating each other on the -$X^{\delta-}$- atom: $F_1 = \delta_1^+\delta_1^-/4\pi\varepsilon\varepsilon_o l_{b1}^2$ and $F_2 = \delta_2^+\delta_2^-/4\pi\varepsilon\varepsilon_o l_{b2}^2$ [20]. The vectors of mechanical moments of these forces are opposite and coincide with the direction of bonds b_1 and b_2. They are proportional to the strength of these bonds and, compensating each other on the -$X^{\delta-}$- atom, they ensure the temporary structural stability of the complex, i.e., insofar as EMCC is in the ESP state.

B. Superficial density of electric charges

Because of the dielectric nature of the complex molecule and the lack of galvanic bond between the δ_1+, δ- and δ_2+ as electrostatic charges distributed with different superficial electrical density (σ) (SFED effect) on the molecular fragments R-, -$X^{\delta-}$- and -Cu^+L. In its essence, the SFED effect is a physical process through which E_p* is manifested as a magnitude which is proportional to the size of σ. In an active polymerization process, owing to quantum mechanical reasons, E_p* is transformed into an activating energy (E_a) which is transferred from the complex towards the monomer in accordance with $\sigma \equiv E_p^* \equiv E_a \equiv nE_a'$ (E_a' – elementary amount E_a, to be bonded n in-number monomer molecules). In this case, subject to discussion is σ of the charges δ_1+ and δ_2+, distributed on different in size molecular fragments R- and -Cu+L (Fig. 1), as this state expresses the physical essence of the ESP effect on EMCC.

By definition, the size of σ at a given charge (q) is reciprocal to the surface (S) on which q has been distributed, i.e. $\sigma = q/S$ [20]. The density σ of the charge δ- localized on -$X^{\delta-}$ is displayed with the expression $\sigma- = \delta-/S_X^{\delta-}$. But since the charge δ- is composed of two components: δ_1- and δ_2-, σ- is also composed of two components: $\sigma_1- = \delta_1-/S_X^{\delta-}$ and $\sigma_2- = \delta_2-/S_X^{\delta-}$, i.e. $\sigma- = \sigma_1- + \sigma_2-$.

Due to the fact that the initiator (alkyl halide) is a comparatively low-molecular compound, on formation of EMCC, the R- fragment has a smaller volume and a smaller surface than the -Cu+L fragment, where L is a higher molecular compound. This is why the density of σ_1+ of the charge δ_1+ induced on R- ($\sigma_1+ = \delta_1+/S_R$) is greater than σ_2+ ($\sigma_2+ = \delta_2+/S_{Cu^+L}$) of the charge δ_2+ induced on -Cu+L, whose surface should be much bigger ($S_{Cu^+L} >> S_R$), i.e. $\sigma_1+ > \sigma_2+$. Therefore, the difference $\sigma_1+ - \sigma_2+ = \Delta\sigma+$ between the σ_1+ and σ_2+ densities is proportional to the difference $\delta_1+ - \delta_2+ = \Delta\delta+$ between the electric charges δ_1+ and δ_2+. The charge Δδ+ is the already defined asymmetrical charge δ* (Δδ+ = δ*) and is proportional to the asymmetrical potential φ* and energy E_p*.

In an electrostatic field, the potential (φ_M) in a given point (M) of the field located at a distance (r) from the field-creating charge (q) is equal to the quotient of the charge size and the distance to the point, i.e. $\varphi_M = q/4\pi\varepsilon or$ [20]. In this particular case (Fig. 1), the potentials (φ_1+ and φ_2+) of charges δ_1+ and δ_2+ induced on R- and -Cu+L have been determined against the potential φ- of the charge δ- on the -$X^{\delta-}$ atom. If the potential φ- is accepted as a base (conventional zero), the degree of energy (in electric equivalent) asymmetry of semipolar bonds b_1 and b_2 may be reported according to -$X^{\delta-}$-, which has been accepted as an electric symmetry center of EMCC.

Analogously to δ- and σ-, φ- is also made up of two components: ($\varphi- = \varphi_1- + \varphi_2-$), where φ_1- is the potential of charge σ_1- with density σ_1-, whilst φ_2- is the potential of charge σ_2- with density σ_2-. Since, in absolute value, $\sigma_1+ = \sigma_1-$, and $\sigma_2+ = \sigma_2-$, in bond lengths l_{b1} and l_{b2}, potential φ_1+ may be presented as: $\varphi_1+ = \varphi_1-/4\pi\varepsilon o l_{b1}$, and potential φ_2+ may be presented as: $\varphi_2+ = \varphi_2-/4\pi\varepsilon o l_{b2}$. Because of the fact that φ-, respectively, φ_1- and φ_2- , have been accepted as base values ($\varphi_1- = 0$ and $\varphi_2- = 0$) used to report φ_1+ and φ_2+, the differences $\varphi_1+ - \varphi_1- = \varphi_1+$ and $\varphi_2+ - \varphi_2- = \varphi_2+$ are in essence the potential differences at the ends of the bonds b_1 and b_2, i.e., φ_1+ at the ends of bond b_1 and φ_2+ at the ends of bond b_2. But since $\sigma_1+ > \sigma_2+$, it follows that $\varphi_1+ > \varphi_2+$. Obviously, as compared to the electric symmetry center -$X^{\delta-}$-, the b_1 bond is polarized to a greater extent than the b_2 bond with the value of the asymmetrical electric potential φ* ($\varphi_1+ - \varphi_2+ = \varphi^*$).

The potential energy E_p and the potential φ are not equivalent; however, they are dependent on each other: $E_p = q\varphi$ [20]. Thus, the equation of the potentials $\varphi_1+ - \varphi_2+ = \varphi^*$ may transform into equation of energies, and E_p* will be assessed by means of the energy of bonds b_1 and b_2. Since the following charges correspond to the potentials φ_1+, φ_2+ and φ*: to $\varphi_1+ \rightarrow \delta_1+$, to $\varphi_2+ \rightarrow \delta_2+$, and to $\varphi^* \rightarrow \delta^*$, hence $\delta_1+\varphi_1^+ = E_{b1}$, $\delta_2+\varphi_2+ = E_{b2}$ and $\delta^*\varphi^* = E_p^*$, from the analogy of potentials follows that $E_{b1} - E_{b2} = E_p^*$ or $E_{b1} > E_{b2}$. Therefore, the energy of bond b_1 is greater than the energy of bond b_2 with the size of E_p*, which, via the SFED effect, is transformed into activating energy E_a of EMCC, i.e. $\sigma_1+ \equiv E_p^* \equiv E_a$.

C. Electrochemical polarization of an active transition metal complex

The DMP hypothesis provides for the occurrence of an electrochemical polarization (ECP) of the organic transition metal complex. It is due to the inner molecular grouping -$X^{\delta-} \leftarrow Cu^+$L, which contains the components of the redox couple $X^{\delta-}/Cu^+$ (Fig. 1). Under the influence of the potential φ* on the semipolar bond b_1, this couple is structurally blocked (inactive). Depending on the atom type (Cl, Br), it possesses a specific redox potential ($\varphi_{o/r}$). In fact, the electrochemical potential of this couple is the previously described potential φ_2+ ($\varphi_{o/r} = \varphi_2+$), which is a quantitative expression of the degree of electrochemical polarization ECP of EMCC.

V. FUNCTIONAL ACTIVITY OF A TRANSITION METAL COMPLEX

A. Electrostatic depolarization in the presence of a monomer

Transition metal complexation in the presence of a monomer is typical for the conditions of ATRP. When mixing the source components: In, Cat, L, and monomer M, an unstable, double-polarized (ESP and ECP) EMCC is obtained (Fig. 1). Since $E_{b1} > E_{b2}$, with the size of E_p* or the potential of the semipolar bond b_1, respectively, being bigger than that of bond b_2 ($\varphi_1+ > \varphi_2+$), a spontaneous tendency towards overcoming the temporary complex instability by means of the physical effect electrostatic depolarization (ESD) occurs. In this process, E_p* is transferred to the monomer in the form of activating energy E_a, in three consecutive steps (Fig. 2).

1) First step of energy transfer

The first step of energy transfer is illustrated on Fig. 2 (pos. 1). It ensures an elementary portion of activating energy (E_{ec}') for electrostatic coordination between the polar monomer molecule (M) and the polar centers ($-C^{\delta 1+}\rightarrow X^{\delta 1-}$) of bond b_1.

2) Second step of energy transfer

The second step of energy transfer has a quantum mechanical nature. Upon sufficient approximation of the σ-electrons of bond b_1 and the π-electrons of the double monomer bond, the electrostatic interaction between the charges ceases to exist {Fig. 2 (pos. 1)}. An exchange interaction {Fig. 2 (pos. 2)} occurs, however, which triggers genuine initiation of polymerization. It runs with transformation of the sp^2 hybridization of carbo-atoms which is typical of the π-bonds of the monomer, up to the sp^3 hybridization which is typical of the σ-bonds of saturated compounds. During the transformation process, a transition Intermolecular Electron-Resonance Structure (IMERS) is formed which possesses a four-member configuration {Fig. 2 (pos. 2)}. IMERS is a short-lived structure which, due to an insufficient number of π-electrons and the presence of a heteroatom ($-X^{\delta-}$) has no aromatic stability and is unstable [1,2].

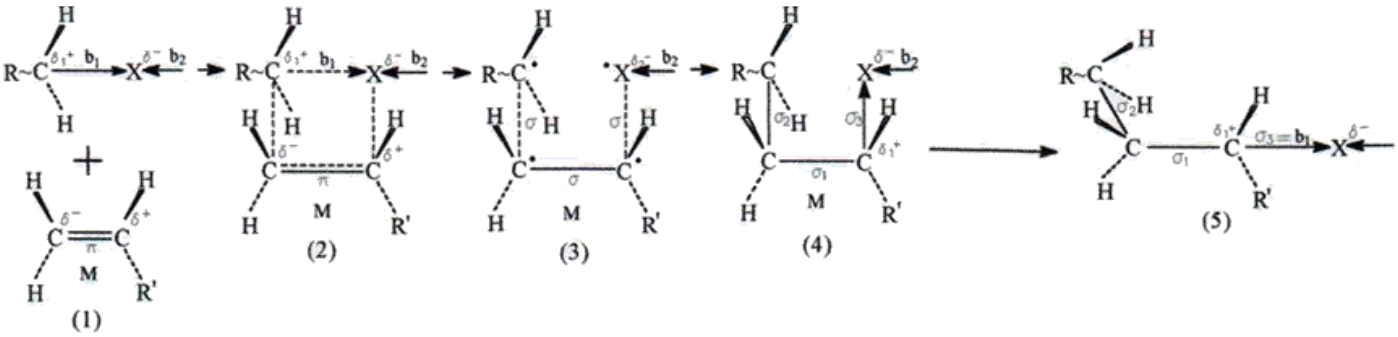

Figure 2. Functional activity of a transition metal complex

Due to the presence of a heteroatom and a bilateral –I effect, S→T/T→S electronic transitions are induced in IMERS. In the S→T transitions, the monomer π-bond and bond b_1 break off and three radical pairs are formed (RP, RPs). The first RP originates from the monomer molecule and is a covalently linked radical pair (biradical $>C^{\bullet}—C^{\bullet}<$) {Fig. 2 (pos. 3)}. The second one is non-covalently (||) linked and is formed between the growing macroradical $R\sim C^{\bullet}H_2$ and the left carbon atom of the biradical ($>C^{\bullet}$-) ($R\sim C^{\bullet}H_2 \parallel >C^{\bullet}$-) (pos. 3). The third one is also non-covalently linked and is formed between the $-X^{\delta-}$- atom and the right carbon atom of the biradical (-C•<) ($-C•< \parallel {}^{\bullet}X^{\delta-}$) (pos. 2). Because of the temporary preservation of the covalent nature of bond b_2, the component ${}^{\bullet}X^{b2-}$ has a partially negative charge δ_2^- and manifests as a short-lived ion-radical ${}^{\bullet}X^{b2-}$ (pos. 3). As a result of the T→S transitions and the recombination between the singlet electrons of the non-covalently linked RPs, with the exception of the σ_1 bond, which is present in the biradical, two new σ bonds are formed - σ_2 and σ_3 {Fig. 3 (pos. 4)}. Bonds σ_1 and σ_2 are normal covalent bonds, but the third one – σ_3, which is under the influence of the $-X^{\delta-}$- atom, is polarized and in fact repairs an already broken off b_1 bond ($\sigma_3 = b_1$) {Fig. 2 (pos. 5)}. Due to the b_1 breakoff and its repair with one monomer unit forward, the monomer joining resembles a process of "insertion" between polar centers $-C^{\delta 1+}\rightarrow X^{\delta 1-}$ of EMCC. Irrespectively of the insertion, fragment $-C^{\delta 1+}$, which is elongated by one monomer unit (m) through the repaired bond b1 remains linked to the halogen atom ($-Cm^{\delta 1+}\rightarrow X^{\delta-}$-) {Fig. 2 (pos. 5)}.

According to the PDFM theory, the ATRP chain growth is the result of a quantum mechanical process. The IMERS role corresponds to the theory of non-adiabatic chemical reactions [21] and tunes well with the mechanisms of quantum mechanical energy transfer between closely situated potential surfaces in the S→T/T→S electronic transitions. This supports the assertion [1,2] that ATRP initiation is due to the quantum mechanical transfer of a portion of the activating energy (E_{gi}') in the transition process.

3) Third step of energy transfer

This step ensures the transfer of quantum mechanical energy (E_{pa}') to overcome the energetically disadvantageous planar conformation energy which would occur in the joining of the last monomer unit to the macro-chain.

Therefore, the total quantity of activating energy (E_a'), necessary for the realisation of the three consecutive steps for energy transfer in an elementary process is the sum of three elementary quantities: $E_a' = E_{ec}' + E_{gi}' + E_{pa}'$.

VI. Destruction of an Active Transition Metal Complex

A. Electrochemical depolarization in the presence of a monomer

Electrochemical depolarization (ECD) of EMCC in the presence of a monomer cannot be presented independently in pure form, separately from the stage of completion of the polymer chain growth which is typical of ATRP. This stage (Fig. 3) is presented in a generalized ATRP functional scheme [1,2]. Polymer chain growth is completed when, due to the completed electrochemical depolarization (ESD), potential φ* becomes equal to zero, bond b_1 breaks off and the redox couple $X^{\delta-}/Cu^+$ is structurally deblocked.

The break-off of the bond b_1 triggers transfer of an electron from $-Cu^+L$ to $-X^{\delta-}$, whereupon $-X^{\delta-}$ is reduced to a state of an ion (X-), which takes the place of an anti-ion in the ATRP-inactive C-x^{II} complex. Since the $-X^{\delta-}$ atom is simultaneously functionally valid both for EMCC and for the $X^{\delta-}/Cu^+$ couple, the processes in both systems are linked and run consecutively. Therefore, oxidation of the Cu^+ atom to a state of Cu^{2+} cannot run spontaneously before completing ESD of EMCC. The electron transfer, however, triggers a structural deblocking of the redox couple $X^{\delta-}/Cu^+$, which is activated, the potential φ_2+ on b_2 drops off ($\varphi_2+ = 0$, $\varphi_{o/r} = 0$) and EMCC (C-x^I) breaks off.

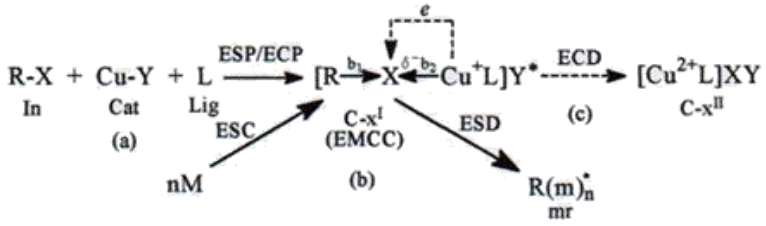

Figure 3. Electrochemical depolarization of a transition metal complex

B. Electrochemical depolarization in the absence of a monomer

Transition metals complexation also exists in the absence of a monomer, which is typical of the ATRA process. In this case, however, under the influence of the instant, simultaneous electrostatic and electrochemical depolarization (ESD and ECD) of EMCC, due to a one-off transfer of electron, the process ends as an ordinary redox reaction: destruction of the complex of low valence form of the transition metal C-x^I, formation of a complex of the oxidized form of the transition metal C-x^{II} and of the dimer product R-R (a C-C bond is formed), whereupon the transition metal complex breaks off.

VII. Conclusion

It proved impossible to present the proposed single physico-chemical theory of transition metal halogen derivatives complexation (TMCPDT) independently, in pure form, completely separately from the ATRP technology. This is because TMCPDT actually covers the ATRP theory in full, no matter which transition metal or technological ATRP variant is concerned.

It was made clear that the abovementioned general conclusion should be added to the attempts to present TMCPDT as a significant complement to the theory of complex compounds and catalytic chemistry, and as an actual functional mechanism of ATRP [1,2], in particular. Metal organic complexes of transition metal halogen derivatives naturally form a standalone group of specifically acting catalysts, defined here as soluble metal organic catalysts, identical with the established scientific terminology. These arguments have an objectively existing justification. They, however, are in no case attempts to compromise the technological achievements in the sphere of ATRP or the theoretical contribution of the creators of this method [5,6]. Yet, TMCPDT does prove that the theoretical fundamentals of ATRP and of the theory of complexation and functional (catalytic) activity of organic complexes of transition metal halogen derivatives do not come down only to the well-known conventional ATRP mechanism. On the contrary, the essence of these fundamentals lies in a specific borderline area between the theoretical aspects of chemistry and physics [22], where TMCPDT actually stands.

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Stefko B. Iliev was born in Pleven, Bulgaria, on December 2nd, 1938. In 1966, he completed his studies at the Higher Medical Institute in Sofia where he obtained the qualification of pharmacist. In 1997, he was awarded the qualification of chemist engineer from the Higher Institute of Chemical Technologies in Burgas, Bulgaria. In 2009, he defended his dissertation titled "Comparative Analysis of the Effects of Continuously and Impulse Magnetic Fields on Radical Polymerization" in Sofia University, Bulgaria, and was awarded a doctoral degree.

In the autumn of 1960, he was demobilized from the army with the qualification of Radio Location Station Operator. He is currently retired. He has been a General Director of the chemical enterprise "Himik" in the Bulgarian town of Razgrad for 22 years. He has published 28 scientific articles and holds 6 patents. Among his articles are "ATRP – polarizing/depolarizing functional mechanism II," published in IJSEI, 7(82), 2018 and "Chemical reactor-polymerizer," published in IJSEI, 8(89), 2019.

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