



On the mechanism of activation of copper-catalyzed atom transfer radical polymerization



Abdirisak Ahmed Isse^{*,1}, Nicola Bortolamei, Patrizia De Paoli, Armando Gennaro¹

Department of Chemical Sciences, University of Padova, Via Marzolo 1, 35131 Padova, Italy

ARTICLE INFO

Article history:

Received 31 January 2013

Received in revised form 26 April 2013

Accepted 27 April 2013

Available online 7 May 2013

Keywords:

ATRP

Inner-sphere electron transfer

Activation mechanism

Dissociative electron transfer

Halogen atom abstraction

ABSTRACT

The mechanism of activation of atom transfer radical polymerization (ATRP) has been analyzed by investigating the kinetics of dissociative electron transfer (ET) to alkyl halides (RX) in acetonitrile. Using a series of alkyl halides, including both bromides and chlorides, the rate constants of ET (k_{ET}) to RX by electrogenerated aromatic radical anions ($A^{\bullet-}$) acting as outer-sphere donors have been measured and analyzed according to the current theories of dissociative ET. This has shown that the kinetic data fit very well the “sticky” dissociative ET model with the formation of a weak adduct held together by electrostatic interactions. The rate constants of activation, k_{act} , of some alkyl halides, namely chloroacetonitrile, methyl 2-bromopropionate and ethyl chloroacetate, by $[Cu^I L]^+$ ($L = \text{tris}(2\text{-dimethylaminoethyl})\text{amine}$, $\text{tris}(2\text{-pyridylmethyl})\text{amine}$, $1,1,4,7,7\text{-pentamethyldiethylenetriamine}$) have also been measured in the same experimental conditions. Comparisons of the measured k_{act} values with those predicted assuming an outer-sphere ET for the complexes have shown that activation by Cu(I) is 7–10 orders of magnitude faster than required by outer-sphere ET. Therefore, the mechanism of RX activation by Cu(I) complexes used as catalysts in ATRP occurs by an inner-sphere ET or more appropriately by a halogen atom abstraction.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Atom transfer radical polymerization (ATRP) is one of the most studied techniques of controlled living radical polymerization. It can be applied to a wide range of monomers for the preparation of many polymers with controlled molecular weights and well-defined architectures [1]. ATRP is typically catalyzed by copper complexes with multidendate N-donor ligands (L). The success of the process mainly relies on the establishment of an equilibrium in which a dormant species bearing a C–X bond (an alkyl halide initiator R–X or a deactivated macromolecular chain $P_n\text{--}X$) reversibly reacts with a metal complex at a low oxidation state (activator) to produce the propagating radical (R^{\bullet}) and the metal at a higher oxidation state (deactivator) (Scheme 1). This equilibrium is highly shifted to the left so that $[R^{\bullet}]$ is very small and as a consequence the contribution of bimolecular radical–radical termination reactions is drastically reduced. The typical values of equilibrium constant (K_{ATRP}) for copper-catalyzed ATRP in polar aprotic solvents are well below 10^{-4} [2–4]. Thus, in ATRP the propagating chains are intermittently activated and deactivated allowing a good control over polymerization. However, since bimolecular termination is not completely suppressed, normal ATRP often requires high

concentrations of catalyst. Some new ATRP techniques, such as activators regenerated by electron transfer ATRP [5], initiators for continuous activator regeneration ATRP [6,7] and electrochemically mediated ATRP [8,9] have been recently developed to overcome this problem. With these techniques well controlled polymerizations can be achieved at very low catalyst concentrations [1,10].

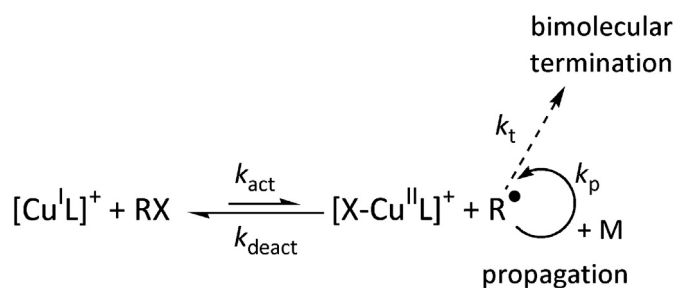
Knowledge of the kinetic and thermodynamic parameters pertaining to the ATRP equilibrium as well as a profound understanding of the reaction mechanism are essential not only for the optimization of the ATRP process, but also for the development of more efficient catalysts. The copper complexes used as catalysts often undergo quite complex speciation in the reaction medium [11]. However, it has been recently shown for the catalytic system $Cu/L/X$ ($L = \text{tris}(2\text{-dimethylaminoethyl})\text{amine}$, $X = Cl^-, Br^-$) in acetonitrile that, although $[Cu^I X_2]^-$, $[XCu^I L]$ and $[Cu^I L]^+$ are present in the reaction mixture, only $[Cu^I L]^+$ reacts with the initiator RX [12]. It is important to note that the ternary complex $[XCu^I L]$ is not a good activator even though on thermodynamic grounds it is a stronger reducing catalyst than $[Cu^I L]^+$ [11].

The mechanism of carbon-halogen bond activation by Cu(I) complexes has been extensively investigated in relation to the initiation step in ATRP [13–20]. It is believed that in ATRP the halogen atom transfer from RX to Cu(I) occurs by an inner-sphere electron transfer (ISET) process involving a transition state in which RX and Cu(I) are bound through a halogen bridge (Scheme 2). However, in principle, a reaction route involving an outer-sphere electron transfer (OSET), followed by association of X^- to Cu(II) is also possible.

* Corresponding author. Tel.: +39 049 8275677.

E-mail address: abdirisak.ahmedisse@unipd.it (A.A. Isse).

¹ ISE member.



Scheme 1. Copper-catalyzed ATRP.

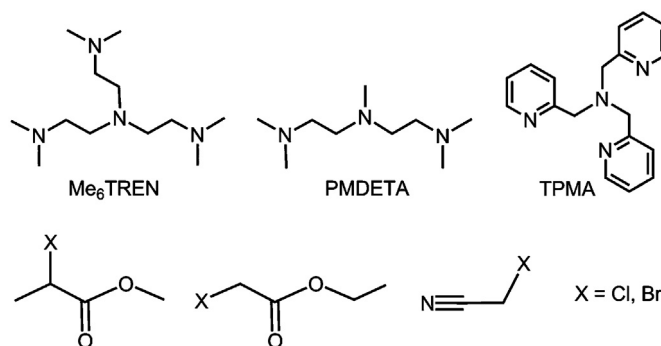
Two possible mechanisms are to be considered for the dissociative electron transfer to carbon-halogen bonds: stepwise mechanism (OSET-SW) involving the formation of a radical anion intermediate $\text{RX}^{\bullet-}$ or a concerted mechanism (OSET-C) in which electron transfer and bond breaking occur in a single step (Scheme 2) [21–24].

Evidence in favor of an ISET mechanism for the activation of RX by Cu(I) complexes has been building up in the literature over the last few years [12,16,18–20]. In particular, it has been shown that electron transfer to alkyl halides of relevance to ATRP never gives $\text{RX}^{\bullet-}$ as an intermediate, the concerted pathway being always the preferred reaction route [18,20]. Therefore, activation through OSET-SW has been safely excluded. Temperature [12,19] and pressure [3] effects on the rate coefficients (k_{act}) of the reaction have shown highly (negative) ΔS^\ddagger and ΔV^\ddagger values reflecting a highly structured transition state, which is not compatible with an outer-sphere electron transfer. In this paper we present a further, definitive evidence that Cu(I) complexes react with RX following an ISET mechanism. This is based on kinetic comparisons between activation rate constants obtained for Cu(I) complexes, typically used as activators in ATRP, and aromatic radical anion donors that react according to an OSET mechanism. The chemical structures of the alkyl halides investigated in this work and the amine ligands (L) used to prepare the copper complexes are shown in Scheme 3.

2. Experimental

2.1. Chemicals

Acetonitrile (Carlo Erba, RS) was purified by distillation over CaH_2 . Tetraethylammonium tetrafluoroborate (Et_4NBF_4 , Alfa Aesar, 99%), used as supporting electrolyte, was recrystallized from ethanol and dried at 70°C under vacuum. Tris(2-dimethylaminoethyl)amine (Me_6TREN) was prepared by methylation of tris(2-aminoethyl)amine (TREN) in a mixture of formaldehyde and formic acid and purified by vacuum distillation



Scheme 3. Molecular structures of L and RX.

[25]. All other compounds were high grade commercial products that were used as received. The copper complexes were always prepared in situ starting from either copper(II) trifluoromethanesulfonate (Aldrich, 98%), or tetrakis(acetonitrile)copper(I) tetrafluoroborate ($\text{Cu}^{\text{I}}(\text{MeCN})_4\text{BF}_4$, Aldrich, 97%). The Cu(I) salt was standardized by spectrophotometric analysis, using 2,9-dimethyl-1,10-phenanthroline as a specific ligand ($\epsilon = 8458 \text{ M}^{-1} \text{ cm}^{-1}$) in a 2-fold excess with respect to the metal [26], whereas standardization of the Cu^{II} salt was performed by iodometric titration.

2.2. Instrumentation

Voltammetric experiments were carried out in a three-electrode cell with a double wall jacket through which water from a thermostated bath (Thermo Scientific, HAAKE SC100) was circulated; all experiments were carried out at $25 \pm 0.1^\circ\text{C}$. An Autolab PGSTAT30 potentiostat/galvanostat (EcoChemie, The Netherlands) run by a PC with GPES software was used. The working electrode was a 3 mm diameter GC disk (Tokai GC-20), whereas the counter and reference electrodes were a Pt ring and $\text{Ag}|\text{AgI}|0.1 \text{ M } n\text{-Bu}_4\text{NI}$ in DMF, respectively. Prior to each experiment the working electrode surface was cleaned by polishing with a $0.25\text{-}\mu\text{m}$ diamond paste, followed by ultrasonic rinsing in ethanol for 5 min. At the end of each experiment the potential of the reference electrode was calibrated against the ferrocenium/ferrocene couple for which $E^\circ_{\text{Fc}^+/\text{Fc}} = 0.390 \text{ V}$ vs. SCE in the solvent/supporting electrolyte used in this work [27]. This allowed conversion of all measured potentials vs. the aqueous saturated calomel electrode.

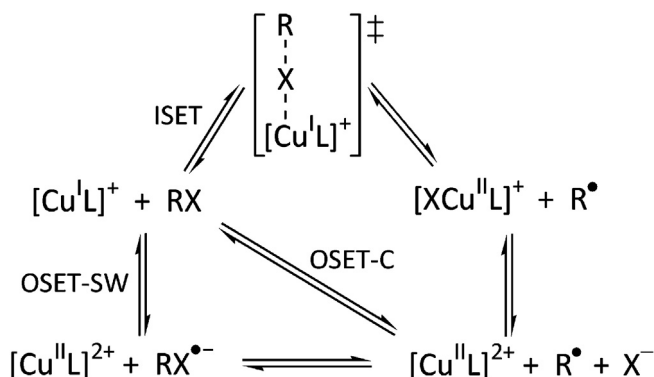
The kinetics of the activation reaction between RX and Cu(I) was followed by chronoamperometric monitoring of Cu(I) oxidation at a rotating disk electrode (RDE, Autolab, Eco-Chemie) with a GC tip disk (3 mm diameter, Metrohm).

DigiSim 3.03 (Bioanalytical Systems) was used to simulate all voltammetric responses necessary for the construction of working curves used to determine rate constants of ET in solution.

3. Results and discussion

3.1. Kinetics of activation of alkyl halides by outer-sphere electron donors

Aromatic and heteroaromatic radical anions, $\text{A}^{\bullet-}$, can be easily electrogenerated from their neutral precursors through a reversible one electron reduction process, characterized by a low reorganization energy thanks to the ability of the radical anions to delocalize the negative charge [28]. These radical anions have also low propensity to form new bonds. For these reasons they are often considered to be outer-sphere electron donors and used for the analysis of the dynamics of homogeneous electron transfer



Scheme 2. Possible mechanisms of RX activation by Cu(I) complexes.

Download English Version:

<https://daneshyari.com/en/article/6615781>

Download Persian Version:

<https://daneshyari.com/article/6615781>

[Daneshyari.com](https://daneshyari.com)