Electrochemical generation and quenching of the metal-to-ligand-charge-transfer (MLCT) excited states in systems containing ruthenium complexes RuL$_3^{2+}$

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Tris(4,7-diphenyl-1,10-phenanthroline)ruthenium(II) Ru(baph)$_3^{2+}$ and tris(2,2'-bipyridine)-ruthenium(II) Ru(bipy)$_3^{2+}$ complexes in mixed systems i.e. with four series organic co-reactants Q in 0.1 M (C$_2$H$_5$)$_4$NPF$_6$ acetonitrile solutions were employed as systems in the electrochemically generated chemiluminescence (ECL) and electron transfer quenching studies. The generation of electroactive species at the electrode by means of the triple-potential-step technique and their annihilation in the mass-controlled region cause production of Metal-to-Ligand-Charge-Transfer (MLCT) excited state of *RuL$_3^{2+}$ and the chemiluminescence to appear. MLCT excited states are formed in electron transfer reactions (ET) with electron donors (nitroaromatic or quinone radical anions and N-methylpyridinium radicals) as well as with electron acceptors (aromatic amine radical cations).

$$\begin{align*}
\text{RuL}_3^{3+/+} + \text{Q}^{\ddagger/\ddagger} & \xrightarrow{k_{sep}} \text{RuL}_3^{3+/+} \text{Q}^{\ddagger/\ddagger} \\
\text{RuL}_3^{3+/+} \text{Q}^{\ddagger/\ddagger} & \xrightarrow{k_{45}} \text{RuL}_3^{3+/+} \text{Q}^{\ddagger/\ddagger}
\end{align*}$$

The yields for the excited state formation can be easily estimated from ECL emission intensities. On the other hand, quenching of the excited states *Ru(bipy)$_3^{2+}$ and *Ru(baph)$_3^{2+}$ with the same organic co-reactants have been studied using steady-state Stern-Volmer approach. The experimentally determined quenching rate constants $k_q$ obtained for all system studied allowed to evaluate kinetic parameters according to the following schemes of the reaction mechanism:

$$\begin{align*}
*\text{RuL}_3^{2+} + \text{Q}^{\ddagger/\ddagger} & \xrightarrow{k_{21}} *\text{RuL}_3^{2+} \text{Q}^{\ddagger/\ddagger} \\
*\text{RuL}_3^{2+} \text{Q}^{\ddagger/\ddagger} & \xrightarrow{k_{45}} *\text{RuL}_3^{2+} \text{Q}^{\ddagger/\ddagger}
\end{align*}$$

Thus, ECL can be described by using the same group of kinetic data as derived from ET quenching. It means that all experimental values of ECL efficiencies should be predictable by means of quenching parameters. The main aim of conducted studies was devoted to such characterization of both ET processes.