# Red photoluminescence in the synthesis of triphenylmethyl radicals by the Gomberg method

**Ramil G. Bulgakov,* Sergei P. Kuleshov and Zemfira S. Valiullina**

*Institute of Petrochemistry and Catalysis, Bashkortostan Republic Academy of Sciences and Ufa Scientific Centre of the Russian Academy of Sciences, 450075 Ufa, Russian Federation. Fax: +7 3472 31 2750*

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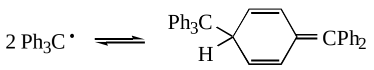
**The red photoluminescence ($\lambda_{max}$ = 580±20 nm) observed in the synthesis of the $Ph_3C^\bullet$ Gomberg radical is assigned to a luminescence of the $(Ph_3C{-}Ph{-}\dot{C}Ph_2)^*$ radical dimer.**

The discovery of the first radical of the $Ph_3C^\bullet$ type (generated in a reaction of $Ph_3CCl$ with metals) gave impetus to a discussion on the nature of radical and molecular species in the equilibrium system $Ph_3C \rightleftharpoons$ dimer. At a later time, NMR spectroscopy was used to disprove certainly a statement on the existence of hexaphenylethane and to show[1] that an equilibrium took place in the absence of $O_2$ (Scheme 1), where the maximum equilibrium concentration was $[Ph_3C^\bullet]$ = 5% at 300 K.



**1**

**Scheme 1**

The properties and composition of the components of the equilibrium system were studied by various techniques (EPR, NMR and UV spectroscopy and elemental analysis). The photoluminescence (PL) method was never used for these compounds, with one exception, where green PL of $Ph_3C^\bullet$ was detected at 90 K. At the same time, PL of $Ph_3C^\bullet$ was observed in studies[3–6] where the radical was generated at 77 K as a result of UV and γ-irradiation of $Ph_3CCl$ and $Ph_3CH$ solutions. This PL disappeared when the irradiated solutions were unfrozen. Recently, we have reported that $Ph_3C^\bullet$ shows a green PL at 300 K in the absence of $O_2$. A green chemiluminescence of redox reactions which generate $(Ph_3C^\bullet)^*$ is also known.[7–9]

This paper is aimed to investigate the PL method for the equilibrium system (Scheme 1) in the course of the reaction of $Ph_3CCl$ with Zn in solutions. $Ph_3CCl$ of CP grade was used after triple recrystallization from hexane. The purity was monitored by PL ($\lambda_{max}$ = 435 nm) and HPLC. The solvents (THF, $CCl_4$ and $Et_2O$ of CP grade, benzene, toluene and hexane of reagent grade and rectified EtOH) and argon purified and dried according to refs. 10 and 7, respectively, were used. The reactions proceeded in a thermostatted cell of a spectrometer under stirring, the mixture was centrifuged before spectral measurements. PL and absorption spectra were recorded in sealed quartz vessels ($l$ = 10 mm, 300 K) or cells ($l$ = 5 mm, 77 K) on a Specord-M40 spectrophotometer and an Aminko-Bowman fluorimeter, respectively.

A decrease in the PL intensity of $Ph_3CCl$ ($\lambda_{max}$ = 435 nm) and the appearance of the PL of $Ph_3C^\bullet$ ($\lambda_{max}$ = 525, 550 nm) were observed after mixing $Ph_3CCl$ (0.18 mmol) with Zn powder (1.56 mmol) at 300 K in Ar (Figure 1). Within 5–10 min, a red PL ($\lambda_{max}$ = 580±20 nm) was observed together with a rise in the intensity of the green PL of $Ph_3C^\bullet$. An absorption spectrum of the solution consists of bands of the radical $Ph_3C^\bullet$ ($\lambda_{max}$ = 334, 516 nm) and $\lambda_{max}$ = 440 nm. In the PL excitation spectra of the solution, for the bands at $\lambda_{max}$(PL) = 525, 550 nm, $\lambda_{max}$ = 334, 516 nm were detected, caused by the $Ph_3C^\bullet$ absorption, and for a band at $\lambda$(PL) 580 nm, $\lambda_{max}$ = 435 nm. These data allowed us to assign a band at $\lambda_{max}$ = 435 nm to the absorption of a product responsible for the red PL. Note that the position of the maximum does not correspond to $Ph_3C^\bullet$ or its molecular dimer having $\lambda_{max}$ = 313 nm. Previously, an absorption band at $\lambda_{max}$ = 430 nm was found in an analogous reaction alongside with the bands of $Ph_3C^\bullet$ though it was not identified. As the reaction proceeded for 30–40 min, the intensities of the bands at $\lambda_{max}$ = 525 and 550 nm were redistributed and the intensity of the red PL increased. At longer reaction times (> 2 h), the green PL disappeared, and the red PL was retained. However, in this case, $Ph_3C^\bullet$ was detected in the solution by its characteristic PL at 77 K. Two reasons for the disappearance of green PL are possible: the quenching of $(Ph_3C^\bullet)^*$ with energy transfer to a product responsible for the red PL ($E_{red}$) and a chemical transformation of $Ph_3C^\bullet$ to this product. We cannot explain now this PL disappearance. The presence of a red PL depends on the nature of the solvent. It does not appear in THF (77, 300 K). In benzene, toluene, $CCl_4$, EtOH or $Et_2O$, a red PL was detected at $\lambda_{max}$ = 580±20 nm. The addition of THF to a toluene solution (having red and green PL) causes selective quenching of the red PL. The red PL was quenched completely at the THF : toluene volume ratio 1:1. A decrease in the intensity and disappearance of the red PL during the addition of THF can be caused by two reasons: radiationless energy transfer from $(E_{red})^*$ to THF and a chemical reaction of the red PL emitter with THF. The fact that red PL is not reduced in a frozen solution evidences a chemical interaction.

$(E_{red})^*$ is more stable to $O_2$ than $(Ph_3C^\bullet)^*$. When an aliquot portion of air is added to the reaction mixture exhibiting green and red PL, the green PL of $Ph_3C^\bullet$ disappears immediately, and the red PL is detected for more than 2 h. However, after passing an air flow for more than 2 h, the red PL also disappears. When $O_2$ is added to a $Ph_3CCl$ solution before the contact with Zn and

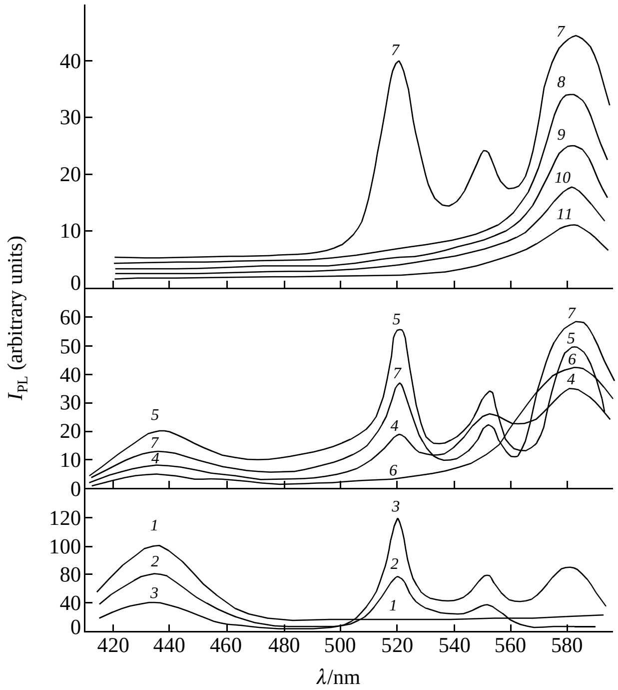
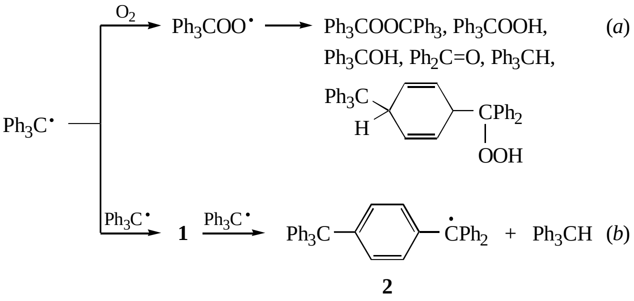


**Figure 1** PL spectra in the reaction $Ph_3CCl$ + Zn: (*1*) and (*2*) THF, 300 K, after 0 and 10 min; (*3*), (*4*) and (*6*) toluene, 300 K after 20, 40 and 60 min; (*5*) and (*7*) toluene, 77 K, after 40 and 60 min; (*8*), (*9*), (*10*) and (*11*) toluene, 77 K, after thawing (*7*) and a single $O_2$ injection (10 ml) and exposure at 300 K for 1, 30, 40 and 30 min, respectively.

then it is bubbled during the reaction, green and red PL are not detected at all, as $Ph_3C^{\cdot}$ is consumed completely[11] to react with $O_2$ [Scheme 2(*a*)]:



**Scheme 2**

Thus, a trityl radical is transformed according to Scheme 2(*b*) in the absence of $O_2$. In the presence of $O_2$ a dimer is not observed, and path 2(*a*) is the case. Hence, $(E_{red})^*$ is not generated in a reaction of $Ph_3C^{\cdot}$ with $O_2$; this fact allows us to exclude the set of reaction products [Scheme 2(*a*)] as $(E_{red})^*$. First of all, $E_{red}$ is a product of the interaction of two radicals $Ph_3C^{\cdot}$. Molecular dimer **1** was found[1] to be a product of this interaction. Intermediate **1** generated in reactions of phenyl radicals with *tert*-butyl sulfide and phenyl *tert*-butyl sulfide is highly reactive and transforms into **2** according to Scheme 2(*b*).[12] A choice between **1** and radical dimer **2** falls on **2** as $E_{red}$. First, molecular dimer species are stable to $O_2$ and exhibit luminescence at shorter waves. Second, the replacement of an H atom in the phenyl ring of $Ph_3C^{\cdot}$ is known to cause a shift of the PL maximum to the red region of a spectrum. The results obtained and the absence of a red PL in initial and final reaction products (molecular dimer species) and in all of the solvents allowed us to propose that **2**, an excited radical dimer, is the emitter of the red PL.

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