Red and green chemiluminescence of Na, Mg, and lanthanide triphenylmethyl derivatives during oxidation by dioxygen and cerium(IV)

R. G. Bulgakov, S. P. Kuleshov, Z. S. Valiullina, and B. A. Mustafin*

Institute of Petrochemistry and Catalysis, Academy of Sciences of Republic of Bashkortostan, and Ufa Scientific Center, Russian Academy of Sciences, 141 prosp. Oktyabrya, 450075 Ufa, Russian Federation. Fax: +7 (347 2) 31 2750

Chemiluminescence (CL) of triphenylmethyl organometallics (TPM), Ph_3CNa, Ph_3CMgCl, and Ph_3CLnCl_2 (Ln = Cd, Eu, and Dy), in THF and toluene during oxidation by O_2 and the $(NH_4)_2Ce(NO_3)_6$ complex was found. The first CL is caused by the luminescence of two emitters: $(Ph_3C^{\cdot})^*$, emitting in the green spectral region (λ_{max} = 524, 550 nm), and an unstable product of substitution of the hydrogen atom in the phenyl ring of the $Ph_3C^{\cdot}$ radical, emitting in the red region (λ_{max} = 580±20 nm). The emitter of the second CL, $Ph_3C^{\cdot}$ *, is generated in the elementary electron transfer from the Ph_3C^- anion to Ce^{IV}, reducing the latter to Ce^{III}.

Key words: chemiluminescence, photoluminescence, trityl radical, sodium, magnesium, and lanthanide organometallics.

Studying the chemiluminescence properties of organometallic compounds containing the Ph_3C group, we observed chemiluminescence of triphenylmethyl derivatives of Na, Mg, and lanthanides (Gd, Tb, Eu, and Dy) during their oxidation by dioxygen and cerium (IV). In this work, we investigated the nature and mechanism of this phenomenon.

Experimental

Triphenyl organometallics (Ph_3CNa, Ph_3CMgCl, and Ph_3CLnCl_2) were synthesized by the reactions of the corresponding metals with Ph_3CCl in THF or toluene in an argon atmosphere.[1] Ph_3CCl was obtained from Ph_3COH by the known procedure[2] followed by recrystallization from hexane. The $(NH_4)_2Ce(NO_3)_6$ complex (hereinafter Ce^{IV}) was obtained by the known procedure.[3] A solution of NaO_2 was prepared by the oxidation of sodium benzophenoneketyl by dioxygen in a THF solution.[4] The concentration of superoxide was determined volumetrically from the volume of O_2 evolved upon treatment of this solution with a $FeSO_4$+HCl mixture.[4] Toluene and THF were purified by the known procedures.[5] Chemiluminescence (CL) was detected on the installation described previously[6] by the addition of an aliquot of the Ce^{IV} complex to a solution of triphenylmethyl organometallics (TPM) in a glass CL-cell in an argon atmosphere or during bubbling of air through the solution. CL spectra were measured with an MUM-2 monochromator or (for weaker CL) with a set of boundary light filters. Photoluminescence (PL) was detected on an Aminco-Bowman spectrofluorimeter and on an instrument based on an MDP-23 double monochromator. After measuring CL, solutions were analyzed by the known procedures[1,7] used for studying the autooxidation of Ph_3CNa and the trityl radical dimer, respectively, and by GC-MS on a Finnigan-4000 spectrometer.

Results and Discussion

Oxidation of TPM with air oxygen in THF or toluene produces CL, whose highest intensity and lifetime differ insignificantly for different TPM under the same conditions (Fig. 1). As visualized in parallel experiments, the initial blood-red color of the solution (due to absorption of Ph_3C^- anions) changes rapidly (~15—20 s) to a yellow color (characteristic of the $Ph_3C^{\cdot}$ radical), followed by decolorization and formation of a white precipitate (the precipitate forms at $[TPM]_0 > 10^{-1}$ mol L^{-1}). These observations agree with the disappearance of the characteristic absorption band of the anion (λ_{max} = 480 nm) and appearance of bands of $Ph_3C^{\cdot}$ (λ_{max} = 334, 516 nm). Thus, this CL system has two kinetic regions, depending on the presence or absence of the Ph_3C^- anion.

The CL spectrum measured in the first temporal region coincides with the PL spectrum of the trityl radical. The CL spectrum in the region of smoother decay of the kinetic curve consists of two components: emission of the radical $(Ph_3C^{\cdot})^*$ in the green spectral region (this CL has previously been observed[8,9] by us for Ph_3CNa and Ph_3CLnCl_2) and red CL with a broad maximum in the region of 580±20 nm (Fig. 2). Both CL components are due to the emission of intermediate autooxidation products, since the green and red PL

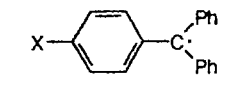
Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 6, pp. 1102—1105, June, 1999.

1066-5285/99/4806-1091 $22.00 © 1999 Kluwer Academic/Plenum Publishers

are absent for the starting and final products (300, 77 K) and appear (77 K) for partially colored solutions of TPM (see Fig. 2). These results contradict the literature data on the assignment of the red CL in the PhMgBr—organic peroxide system to emission of $(Ph_3C^{\cdot})^*$ [10] or $(Eu^{3+})^*$ during oxidation of Ph_3CLnCl_2,[11] because it is known[8,9,12,13] that $(Ph_3C^{\cdot})^*$ luminesces in the green region, and the red CL is observed for derivatives of other lanthanides that do not possess red luminescence.

Radical **1**, the product of replacement of the H atom in the phenyl ring of the trityl radical by another trityl radical or other substituent, *e.g.*, Ph or O, is the most probable emitter of red CL. This assumption is confirmed by both the data[14] on a substantial red shift of the PL spectrum of the trityl radical during replacement of the H atom and identification of such derivatives among the products of autooxidation of $Ph_3C^{\cdot}$ and its dimer.[7]

Existence of kinetic regions of CL suggests a possibility for the Ph_3C^- anion to participate in processes resulting in CL in the first region. Let us consider reactions that can act as potential photostages in the first kinetic region. Excitation of the $Ph_3C^{\cdot}$ radical at the stage of electron transfer to the O_2 molecule from the Ph_3C^- anion bound to the metal in TPM (reaction (1)) is impossible due to the energy deficiency of this reaction.



1

X = Ph_3C, Ph, O

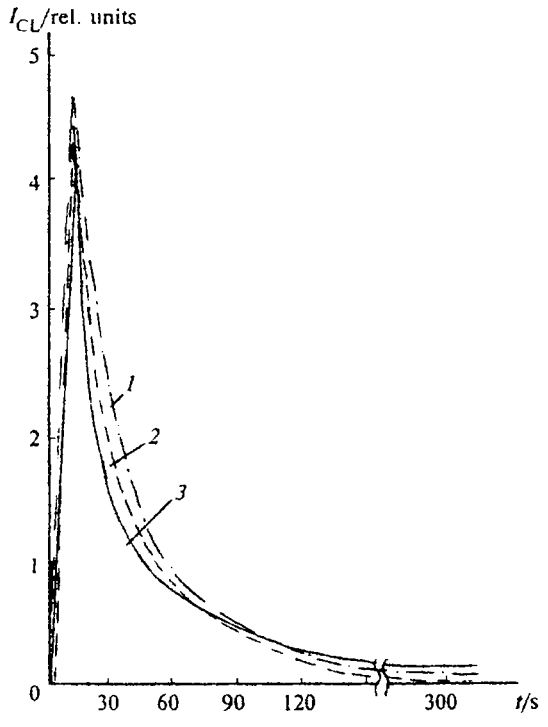
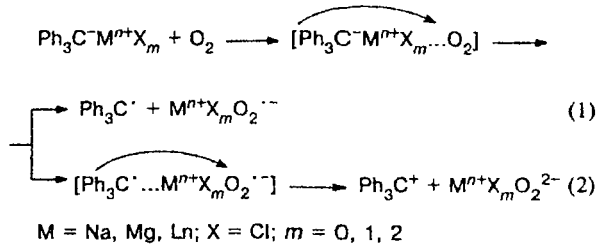


Fig. 1. Time dependences of the CL intensity during autooxidation of TPM ($3 \cdot 10^{-2}$ mol L^{-1}) in toluene (300 K): *1*, Ph_3CNa; *2*, Ph_3CMgCl; and *3*, Ph_3CNa.



The thermal effect of reaction (1), calculated using the electrochemical redox potentials,[15,16]

$$\Delta H = E_1(O_2^-/O_2) - E_2(Ph_3C^-/Ph_3C^{\cdot}) = 0.564 - (-1.09) = 1.654 \text{ eV},$$

does not provide population of the excited state of $Ph_3C^{\cdot}$ (2.37 eV). The radical formed in reaction (1) can be oxidized to the Ph_3C^+ cation due to the transfer of

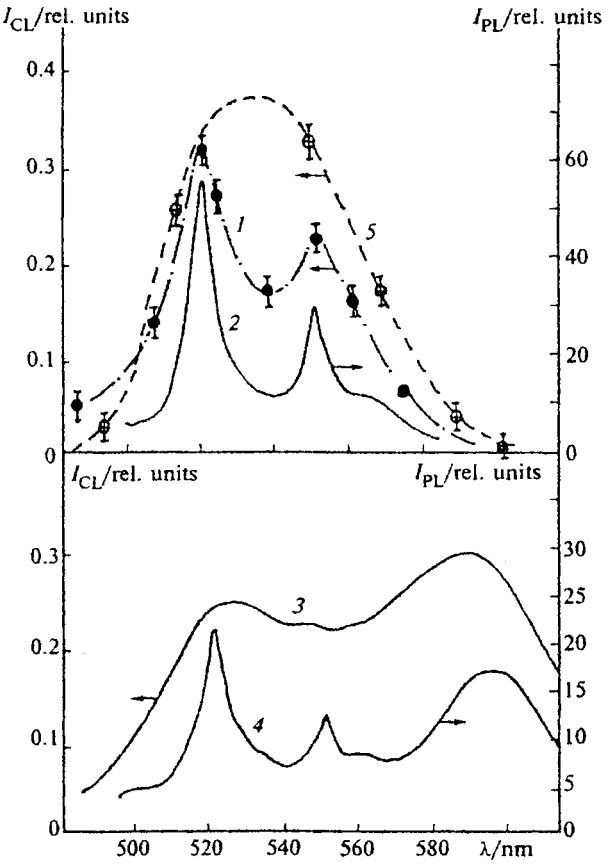


Fig. 2. CL (*1*, *3*, *5*) and PL spectra (*2*, *4*) during oxidation of solutions of TPM ($3 \cdot 10^{-1}$ mol L^{-1}) in toluene (300 K): *1* and *3*, air O_2, regions *a* and *b*, respectively (see Fig. 1); *2* and *4*, solution of $Ph_3C^{\cdot}$ ($6 \cdot 10^{-4}$ mol L^{-1}) obtained according to Ref. 18; *5*, Ce^{IV} oxidant (10^{-2} mol L^{-1}).

the second electron from $Ph_3C^{\cdot}$ to the superoxide O_2^- anion in the composition of the metal peroxide (Eq. (2)), which follows from the value of the thermal effect of this exothermic reaction

$$\Delta H = E_1(O_2^{2-}/O_2^-) - E_2(Ph_3C^{\cdot}/Ph_3C^+) = \\ = 1.72 - 0.48 = 1.24 \text{ eV}.$$

The cation is capable of reacting with the original anion:

$$Ph_3C^+ + Ph_3C^-M^{n+}X_m \longrightarrow [Ph_3C^+...Ph_3C^-M^{n+}X_m] \longrightarrow \\ \longrightarrow M^{n+}X_m + 2\,Ph_3C^{\cdot} \qquad (3)$$

However, comparison of the values of the heat effect of reaction (3)

$$\Delta H = E_1(Ph_3C^{\cdot}/Ph_3C^+) - E_2(Ph_3C^-/Ph_3C^{\cdot}) = \\ = 0.47 - (-1.09) = 1.56 \text{ eV}$$

and the energy of the emitting level of the radical (2.37) shows that the energy deficiency is 0.87 eV, *i.e.*, this reaction does not also result in the formation of $(Ph_3C^{\cdot})^*$. It can be assumed that the interaction of Ph_3C^- with metal peroxide

$$Ph_3C^-M^{n+}X_m + M^{n+}X_mO_2^{\cdot -} \longrightarrow \\ \longrightarrow [Ph_3C^-M^{n+}X_m...M^{n+}X_mO_2^{\cdot -}] \longrightarrow \\ \longrightarrow Ph_3C^{\cdot} + (M^{n+}X_m)_2O_2 \qquad (4) \\ \longrightarrow (Ph_3C^{\cdot})^* \qquad (5)$$

is the most probable photostage to provide the generation of $(Ph_3C^{\cdot})^*$ involving the Ph_3C^- anion.

First, the thermal effect (reactions (4), (5))

$$\Delta H = E_1(O_2^{2-}/O_2^-) - E_2(Ph_3C^-/Ph_3C) = \\ = 1.72 - (-1.09) = 2.81 \text{ eV}$$

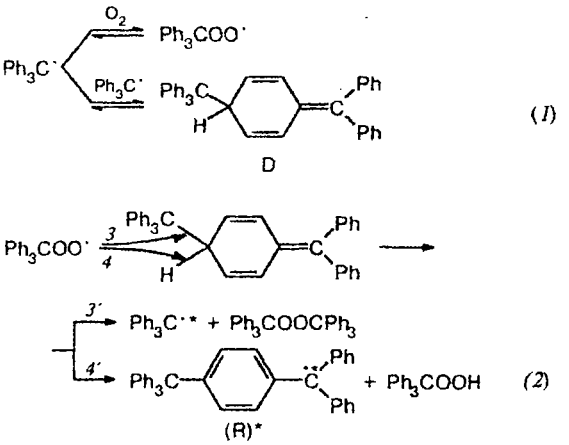
is sufficient for the formation of $(Ph_3C^{\cdot})^*$. Second, modeling of this process by the interaction of NaO_2 with Ph_3CNa gave a positive result as the appearance of CL, whose emitter is also $(Ph_3C^{\cdot})^*$. In addition, we cannot rule out the possibility of excitation of $Ph_3C^{\cdot}$ due to the sequence of processes

$$Ph_3C^{\cdot} + O_2 \longrightarrow Ph_3COO^{\cdot} \xrightarrow{Ph_3C^-M^{n+}X_m} \\ \longrightarrow Ph_3C^{\cdot} + M^{n+}X_m + Ph_3COO^- \\ \longrightarrow (Ph_3C^{\cdot})^* \qquad (6)$$

Unfortunately, it is difficult to estimate the thermal effect (reaction (6)) because data on the redox potentials of the $Ph_3COO^-/Ph_3COO^{\cdot}$ pair are scarce.

In the second region of the kinetic curve, CL is produced by reactions that do not involve the Ph_3C^- anion because it has already been transformed into $Ph_3C^{\cdot}$. The latter is detected in the solution by the characteristic absorption bands during the whole period of CL emission. The products of autooxidation of all TPM contain the compounds $Ph_3COOCPh_3$, Ph_3COH, Ph_3CH, Ph_2CO, and $Ph_3C—Ph—C(Ph)_2OOH$, which are also formed by the autooxidation of the trityl radical dimer,[7,17] which indicates that the mechanisms of these reactions resemble each other. According to the data[18] on dark autooxidation of the dimer (D), two main routes of consumption of $Ph_3C^{\cdot}$ can be pointed out: the transformation into the peroxyl radical in the reaction with O_2 and dimerization (Scheme 1, transformations *1* and *2*).

Scheme 1



Reaction (*1*) is reversible ($K = 8 \cdot 10^3$ mol L^{-1}), and its rate is much higher than that of dimerization.[19] Therefore, both products are present in the reaction solution: the dimer (in a lower amount) and peroxide radicals (in a predominant amount), which interact with each other.[7,17,18] The attack of the dimer by the peroxyl radicals at the C—C and C—H bonds is possible (see Scheme 1, reactions *3*, *3′* and *4*, *4′*). In the first case, $(Ph_3C^{\cdot})^*$ forms, and in the second case, the emitter of red CL, $(R)^*$, forms. The role of the attacking reactant can be accomplished[7] not only by the $Ph_3COO^{\cdot}$ radical, but also by a more complex $ROO^{\cdot}$ radical, to form products similar to those in reactions *3*, *3′* and *4*, *4′*.

To finally identify the emitter of red CL and photostages during TPM autooxidation, we can perform CL modeling for the autooxidation of the trityl radical and reveal the influence of additives of the starting reactants and final products of the oxidation of TPM with dioxygen.

The primary stage of electron transfer to O_2 during TPM oxidation does not result in the excitation of the trityl radical, whereas in the second CL system, the one-electron transfer to Ce^{IV} generates precisely

$(Ph_3C^{\cdot})^*$. The CL of singlets of aromatic molecules generated in the reaction of the electron acceptor Ce^{IV} with sodium anthracenide and pyrenide has previously been reported.[20]

Emission of radicals in solutions at room temperature is a unique phenomenon.[21] Therefore, it was of interest to study the possibility of formation (in a similar electron transfer reaction with the same oxidant) of an electron-excited radical rather than a molecular product (reactions (7)—(10)).

$$Ph_3CNa + Ce^{IV} \longrightarrow (Ph_3C^{\cdot})^* + Ce^{III} + Na^+ \quad (7)$$

$$Ph_3CMgCl + Ce^{IV} \longrightarrow (Ph_3C^{\cdot})^* + Ce^{III} + MgCl^+ \quad (8)$$

$$Ph_3CLnCl_2 + Ce^{IV} \longrightarrow (Ph_3C^{\cdot})^* + Ce^{III} + LnCl_2^+ \quad (9)$$

$$(Ph_3C^{\cdot})^* \longrightarrow Ph_3C^{\cdot} + h\nu \quad (10)$$

In fact, when equimolar (10^{-2} mol L^{-1}) THF solutions of Ph_3CNa, Ph_3CMgCl, or Ph_3CLnCl_2 (Ln = Tb, Pr, and Sm) and $(NH_4)_2Ce(NO_3)_6$ were mixed, we observed CL in the form of a rapidly descending curve. For example, for the reaction of Ph_3CNa, ΔI = 50% over 20 s, $I_{max} = 4.5 \cdot 10^6$ photon s^{-1} mL^{-1}. The CL spectrum measured by boundary light filters on the descending branch of the kinetic dependence of CL intensity is detected in the region of 480—580 nm and correlates with the PL spectrum of the trityl radical (λ_{max} = 524, 550 nm) obtained by the reaction of zinc metal with Ph_3CCl [18] (see Fig. 2). The thermal effect of reactions (7)—(9), calculated using the electrochemical redox potentials

$$\Delta H = E[Ce^{III}/Ce^{IV}] - E[Ph_3C^-/Ph_3C^{\cdot}] = [1.70 - (-1.09)] = 2.79 \text{ eV},$$

provides excitation of $Ph_3C^{\cdot}$ (2.37 eV). Thus, the emitter of this CL, $(Ph_3C^{\cdot})^*$, forms in the elementary act of electron transfer in reactions (7)—(10).

References

1. W. E. Bachman and F. Y. Wiselogle, *J. Am. Chem. Soc.*, 1936, **58**, 1943.
2. L. Fizer and M. Fizer, *Reagenty dlya organicheskogo sinteza* [*Reagents for Organic Synthesis*], Ed. I. L. Knunyants, Mir, Moscow, 1970, 3, 417 pp. (Russ. Transl.).
3. Yu. V. Karyakin and I. I. Angelov, *Chistye khimicheskie veshchestva* [*Pure Chemical Substances*], Khimiya, Moscow, 1974, 408 pp. (in Russian).
4. I. I. Vol'nov, *Peroksidnye soedineniya shchelochnykh metallov* [*Peroxide Compounds of Alkali Metals*], Nauka, Moscow, 1980, 160 pp. (in Russian).
5. A. J. Gordon and R. A. Ford, *Chemist's Companion. A Handbook of Practical Data, Techniques, and References*, Wiley Interscience, New York, 1972.
6. R. G. Bulgakov, V. P. Kazakov, and G. A. Tolstikov, *Khemilyuminestsentsiya metallorganicheskikh soedinenii* [*Chemiluminescence of Organometallics*], Nauka, Moscow, 1989, 220 pp. (in Russian).
7. J. Karen, H. S. Hochser, and J. M. McBride, *J. Am. Chem. Soc.*, 1974, **96**, 4301.
8. R. G. Bulgakov, G. Ya. Maistrenko, B. A. Tishin, G. A. Tolstikov, and V. P. Kazakov, *Dokl. Akad. Nauk SSSR*, 1989, **304**, 1166 [*Dokl. Chem.*, 1989 (Engl. Transl.)].
9. S. P. Kuleshov, R. G. Bulgakov, V. P. Kazakov, and G. A. Tolstikov, *Izv. Akad. Nauk, Ser. Khim.*, 1992, 762 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1992, **41**, 597 (Engl. Transl.)].
10. P. H. Bolton and D. R. Kearns, *J. Am. Chem. Soc.*, 1974, **96**, 4651.
11. G. Ya. Maistrenko, Ph. D. (Chem.) Thesis, In-t Org. Khim. BNTs UrO AN SSSR, Ufa, 1981, 117 pp. (in Russian).
12. T. Izumida, Y. Tanabe, T. Ichinawa, and H. Yoshida, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 235.
13. D. N. Shigorin and Yu. I. Kozlov, *Optika i Spektroskopiya* [*Optics and Spectroscopy*], 1961, **10**, No. 6, 600 (in Russian).
14. V. G. Plotnikov and V. A. Smirnov, *Usp. Khim.*, 1986, **55**, 1633 [*Russ. Chem. Rev.*, 1986, **55** (Engl. Transl.)].
15. S. D. Razumovskii, *Kislorod — elementarnye formy i svoistva* [*Oxygen: Elementary Forms and Properties*], Khimiya, Moscow, 1979, 304 pp. (in Russian).
16. G. Kothe, W. Summermann, H. Baumgartel, and H. Zimmermann, *Tetrahedron*, 1972, **28**, 5949.
17. J. M. McBride, *Tetrahedron*, 1974, **30**, 2009.
18. U. Uoters, *Khimiya svobodnykh radikalov* [*Chemistry of Free Radicals*], Ed. Ya. K. Syrkin, Izd-vo Inostr. Lit., Moscow, 1948, 319 pp. (in Russian).
19. J. A. Howard and K. U. Ingold, *Can. J. Chem.*, 1968, **46**, 2655.
20. R. G. Bulgakov and B. A. Tishin, *Izv. Akad. Nauk, Ser. Khim.*, 1997, 609 [*Russ. Chem. Bull.*, 1997, **46**, 589 (Engl. Transl.)].

Received July 10, 1998