

Chemiluminescence of organometallic compounds in reactions with the free radical galvinoxyl

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Chemiluminescence (CL) is observed in reactions of the free radical galvinoxyl (RO^{\cdot}) with PhMgBr , PhMnCl , $\text{PhTi}(\text{Bu}^{\cdot}\text{O})_3$, and sodium naphthalenide or sodium anthracenide during their oxidation with air and in reactions of RO^{\cdot} with the initial organometallic compounds.

Key words: chemiluminescence, photoluminescence, free radicals.

Usually, the intensity of chemiluminescence (CL) during oxidation of organometallic compounds (OMC) decreases sharply upon introduction of galvinoxyl (1), an effective inhibitor, in a reaction solution and then is partially restored after the complete consumption of 1 in reactions with intermediate radicals. This was demonstrated by us in oxidation of alkylaluminums and alkylborons with $\text{O}_2^{1,2}$ or XeF_2^{3} . However, the addition of compound 1 can also cause a reverse effect, a jump increase in CL intensity.

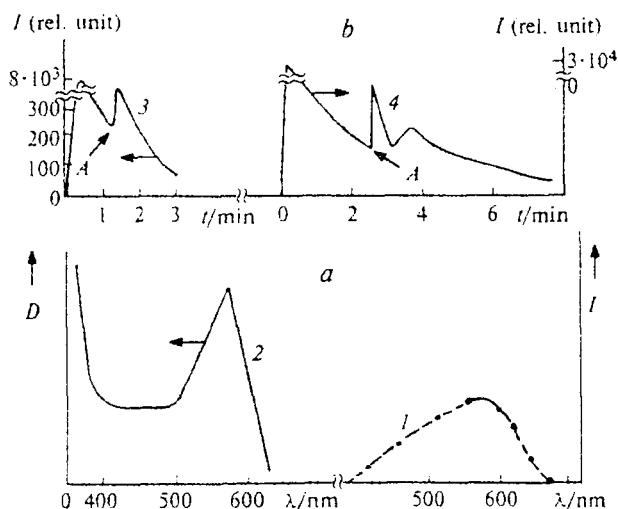
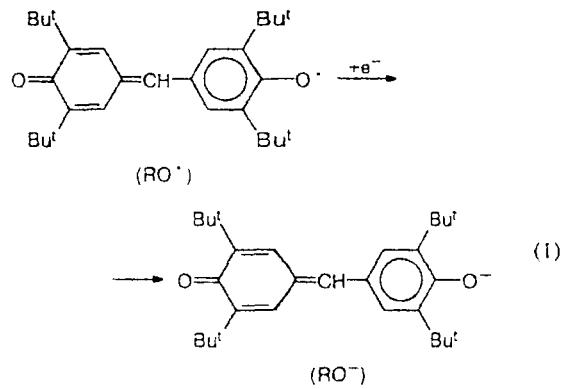


Fig. 1. Spectral (a) and kinetic (b) characteristics of CL in reactions of OMC with the free radical galvinoxyl in THF: 1, a CL spectrum appeared after galvinoxyl ($2.6 \cdot 10^{-3} \text{ mol L}^{-1}$) was added to the reaction solution of sodium anthracenide ($6 \cdot 10^{-3} \text{ mol L}^{-1}$), through which air is bubbled; 2, the absorption spectrum of this solution; 3, PhMnCl ($4 \cdot 10^{-2} \text{ mol L}^{-1}$), through which air is bubbled; 4, PhMgBr ($5 \cdot 10^{-2} \text{ mol L}^{-1}$), through which air is bubbled. The moment when galvinoxyl ($2 \cdot 10^{-4} \text{ mol L}^{-1}$) was introduced is marked with arrow A.

The syntheses of 1 and OMC were described in Refs. 1 and 4, and the methods for measurements of CL and fluorescence (FL) were described in Refs. 2 and 4.

Enhancement of CL during autoxidation of a series of OMC such as PhMgBr , PhMnCl , $\text{PhTi}(\text{Bu}^{\cdot}\text{O})_3$, and $\text{Na}^+\text{X}^{\cdot-}$ (where $\text{X}^{\cdot-}$ is naphthalenide or anthracenide anion-radical) (Fig. 1) appears as a flash of light over the light background observed before the introduction of 1, i.e., not only an increase in CL brightness but also a change in CL kinetics takes place. If the increase in CL intensity were due to energy transfer to compound 1 with its subsequent emission, the shape of the kinetic CL curves would remain unchanged. This attests to the chemical nature of the increase in glow brightness. After compound 1 was introduced in a reaction solution of OMC, the solution turns crimson, and an intense band with $\lambda_{\text{max}} = 580 \text{ nm}$ (Fig. 1) appears in the absorption spectrum, which is characteristic of a phenoxide anion ($\text{RO}^{\cdot-}$), a product of the reduction of 1.⁴

A CL flash is observed not only upon introduction of 1 in reaction solutions of OMC, but also when the initial OMC are mixed with 1 in an atmosphere of argon; that is why both OMC themselves and unstable oxidation products can serve as reducing agents in reaction (1).



The brightest CL is registered for Na^+X^- , which are stronger electron donors.

The CL spectrum measured using an MZD-2M monochromator and corrected for self-absorption of the reaction solution has a maximum at 590 nm (Fig. 1) and correlates well with the FL spectrum of the phenoxide anion,³ which was obtained during the low-temperature (77 K) photoirradiation of a solution of 1 in an ether—isoctane mixture. From this it follows that the excited phenoxide anion (RO^-)^{*} resulting from the electron transfer reaction



is a CL emitter.

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Reactions of 1-aryl-2-bromodiazene 1-oxides with acids and bases

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The reactions of 1-aryl-2-bromodiazene 1-oxides with HCl in nonaqueous media give aryl diazonium chlorides, while 1,3,3-substituted triazenes-1 are formed in the reactions with secondary amines. Using 2-{¹⁵N} label, it was shown that the aryl group does not migrate in these reactions.

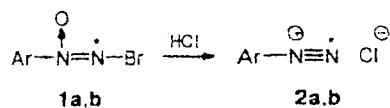
Key words: 1-aryl-2-bromodiazene 1-oxides, diazonium salts, triazenes, ¹⁵N NMR spectroscopy.

Recently,¹ we obtained 1-aryl-2-bromodiazene 1-oxides (BDO) by the reactions of aryl nitroso compounds with NH_4Br in the presence of *N*-bromosuccinimide. Their reactions with olefins were studied. In this work, the reactions of BDO with some acids and bases are studied.

1-Aryl-2-bromodiazene 1-oxides **1** react with HCl in Et_2O to form aryl diazonium chlorides **2** (Scheme 1). Their structure was confirmed by azo coupling with β -naphthol yielding the corresponding compounds. Due to high yields of products **2**, the reaction of BDO with HCl can be used for preparing diazonium salts in nonaqueous media, including preparation from weakly basic amines.

Based on the result of this reaction with 2-{¹⁵N}-**1a** (synthesized by the reaction of nitrobenzene with

Scheme 1



a: Ar = Ph (**2a**, including the sample labeled by ¹⁵N, yield 95%),

b: Ar = 2,4,6-Br₃C₆H₂ (**2b**, 92%)

¹⁵NH₄Br), we can exclude the mechanisms associated with the migration of the aryl substituent. Phenyl-diazonium chloride ¹⁵N-**2a** obtained via Scheme 1 was