

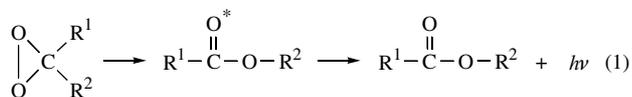
Chemiluminescence occurring upon decomposition of dimethyldioxirane adsorbed from the gas phase onto a silipor surface in the presence of tris(bipyridine)ruthenium(II) and 9,10-diphenylanthracene

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Chemiluminescence arising upon decomposition of dimethyldioxirane adsorbed from the gas phase onto a silipor surface containing tris(bipyridine)ruthenium(II) and 9,10-diphenylanthracene has been found and some mechanisms of activation have been suggested.

One of the most attractive and interesting properties of such powerful oxidizing reagents as dioxiranes (for example, see refs. 1–3) is their chemiluminescence. Indeed, it was previously assumed that upon isomerization of dioxiranes ($H^0 > 356 \text{ kJ mol}^{-1}$) the formation of a triplet excited ester was possible.⁴



Recent experimental investigations have completely confirmed this assumption. Thus, it was found that decomposition of dimethyldioxirane (DMD) in an oxygen-free acetone solution was accompanied by light emission.⁵ The same phenomenon was observed upon interaction of dioxiranes with tris(bipyridine)ruthenium(II) [Ru(bipy)₃]⁶ and some aromatic hydrocarbons.^{2,7} In addition, dioxirane as intermediate has been postulated as a source of chemiluminescence in a number of chemical^{8,9} and biochemical¹⁰ systems.

Recently, we were able to show that isomerization of DMD adsorbed from the gas phase onto a silipor surface is also accompanied by chemiluminescence.¹¹ Since the adsorption of luminescent compounds is known to substantially change their photophysical properties,¹² the latter observation offers a quite new and promising direction in the investigation of the luminescent properties of dioxiranes. In this connection, in the present work some features of chemiluminescence in the system DMD_{abs}-silipor are considered and the significant increase in chemiluminescence intensity in the presence of Ru(bipy)₃ and 9,10-diphenylanthracene (DPHA) placed on the silipor surface is reported for the first time.

The luminescence was recorded as follows. DMD solution (2 ml) in acetone ([DMD]₀ = 6 × 10⁻² mol dm⁻³) was introduced into a cell connected to another cell (V = 27 ml) containing 100 mg of silipor (Silipor 400, Chemapol, 0.125–0.160 mm, 400 m² g⁻¹) and placed above the photocathode of a FEU-140 photomultiplier. An argon flow entering the first cell captured the acetone vapour with the DMD, and this mixture entered the second cell, which was thermostatted at the required temperature. The argon flow was then stopped and chemiluminescence was recorded under static conditions. DPHA and Ru(bipy)₃ were sorbed on silipor as described in ref. 13.

Thus, upon decomposition of DMD on a silipor surface chemiluminescence is observed (maximum intensity of chemiluminescence at 75 °C is equal to 5.7 × 10⁶ photon s⁻¹). The chemiluminescence emitter (estimated by means of light filters) was found to be triplet excited methyl acetate (MA_T^{*}, λ_{max} = 390 nm, see ref. 14). The kinetics of chemiluminescence decay follow an exponential law. It is interesting to note that the rate constant of luminescence decay $k_{cl} = 0.01 \text{ s}^{-1}$ hardly depends on temperature (65–90 °C). From our point of view this is associated with the fact that k_{cl} is an effective value, which depends [apart from reaction (1)] on the adsorption–

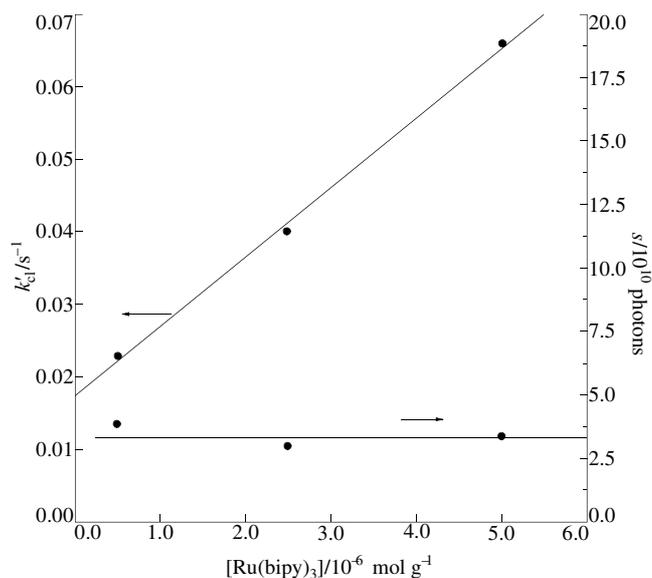


Figure 1 The dependence of k'_{cl} and the light total on Ru(bipy)₃ concentration (75 °C) during DMD_{abs} decomposition on a silipor surface.

desorption equilibrium of DMD. An increase in the efficiency of DMD desorption from the silipor surface with an increase in temperature obviously compensates for the increase in the rate constant of isomerization reaction (1), which results in a constant value for k_{cl} . The chemiluminescence yield (η_{cl})[†] upon decomposition of DMD (the light sum $S = 7 \times 10^8$ photons, 75 °C) adsorbed from the gas phase on the silipor surface is equal to 4 × 10⁻⁹ Einstein mol⁻¹ and the excitation yield (η^*)[‡] of MA_T^{*} is 10⁻⁴. It should be pointed out that η_{cl} , estimated by us, is the lowest possible, because we have assumed that the whole quantity of DMD is adsorbed on a sorbent surface. However, this part can amount to only several percent and in reality the value of η_{cl} should be much higher. One can assume that decomposition of chromophore-containing dioxiranes^{15,16} (for example, dimesityldioxirane or diphenyldioxirane), whose phenyl derivatives possess a greater radiation efficiency, can give us the possibility of observing much brighter chemiluminescence.

The value of chemiluminescence yield in the system DMD_{abs}-silipor is nearly two orders of magnitude higher than that obtained by us when investigating DMD decomposition in

[†] DMD exists only as an acetone solution.^{1–3} Since DMD solutions in acetone are distilled with hardly any fractionation,¹ in order to calculate the DMD concentration in the gas phase we have assumed that the density of DMD and acetone vapours are equal to each other.

[‡] There are no data in the literature concerning the radiative efficiency of MA_T^{*}. Therefore, to calculate its excitation yield we have assumed that the phosphorescence yield of methyl acetate (η_{rad}) is at least no higher than that of related compounds, i.e. ketones: 10⁻³.

