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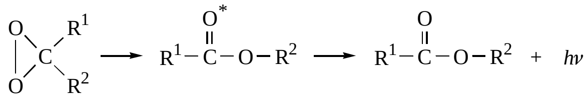
Chemiluminescence arising upon decomposition of dimethyldioxirane adsorbed from the gas phase onto a silipor surface containing tris(bipyridine)ruthenium(II) and 9,10-diphenylanthracene has been found and some mechanisms of activation have been suggested.

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 ($\Delta H^0 > 356$ kJ mol^{-1}) the formation of a triplet excited ester was possible.[4]



$$R^1-\overset{O^*}{\overset{\parallel}{C}}-O-R^2 \longrightarrow R^1-\overset{O}{\overset{\parallel}{C}}-O-R^2 + h\nu \quad (1)$$

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 biochemical[10] 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 ($[DMD]_0 = 6\times10^{-2}$ 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 m^2 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 5.7×10^6 photon s^{-1}). The chemiluminescence emitter (estimated by means of light filters) was found to be triplet excited methyl acetate (MA^*_T, $\lambda_{max} = 390$ 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 $k_{cl} = 0.01$ 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–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 decompostion of DMD (the light sum $S = 7\times10^8$ 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.

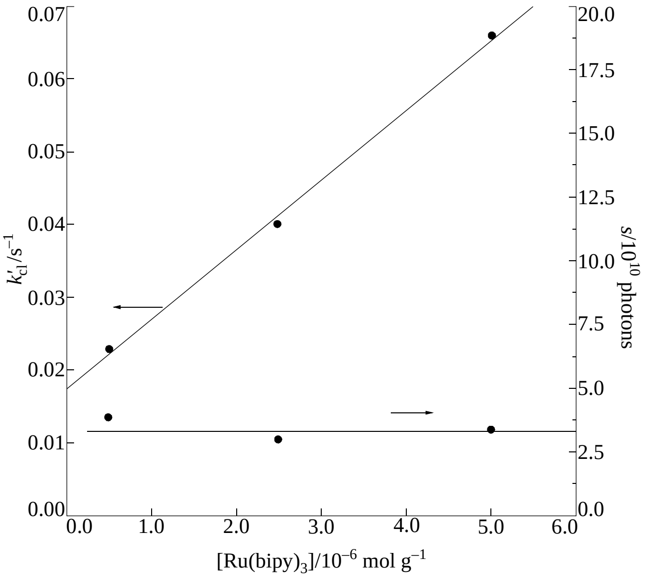


Figure 1 The dependence of k'_{cl} and the light total on $Ru(bipy)_3$ concentration (75 °C) during DMD_{abs} decomposition on a silipor surface.

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

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[†] 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^{-5}.

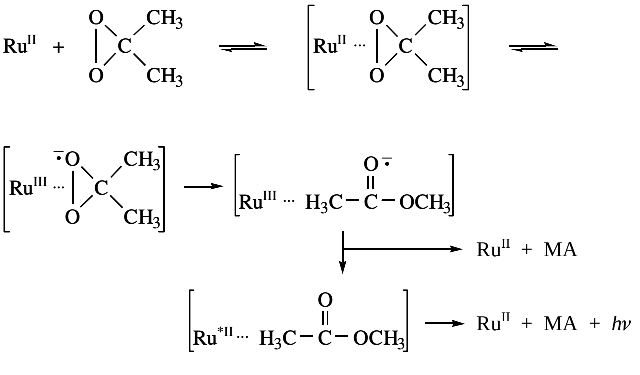
oxygen-free acetone solutions.[5] Obviously, this is associated with the favourable conditions for chemiluminescence on a sorbent surface (for example, the absence of quenching by solvent and different impurities in solution). The other reason obviously lies in the mechanism of DMD decomposition itself. In fact, in solution (without oxygen) DMD is mainly decomposed by a radical-chain mechanism[5,17] ('dark' reaction). That part of chemiluminescent reaction (1) is negligible.[5] Instead, on a sorbent surface the radical-chain processes are not so effective and the isomerization reaction plays a major role in DMD decomposition, which results in a significant increase in chemiluminescence yield.

In the presence of $Ru(bipy)_3$ adsorbed on the silipor surface, a significant increase in chemiluminescence intensity is observed. Thus, at 75 °C and $[Ru(bipy)_3]_0 = 1\times10^{-6}$ mol g^{-1} the maximum intensity of luminescence increases by a factor of 100. The luminescence emitter was found to be $Ru(bipy)_3$. However, in contrast to the DMD decomposition on non-activated silipor, the kinetics of chemiluminescence damping in the presence of $Ru(bipy)_3$ have a more complicated character: a rapid exponential drop in the chemiluminescence intensity followed by a much slower exponential decay. The maximum luminescence intensity on the second (slow) part is about 10% of that on the first (rapid) one. One can suppose that it is the rapid part of the kinetic curve that reflects DMD decomposition, whereas luminescence on the slow part is obviously caused by decomposition of labile compound, formed during oxidation of the complex by the dioxirane.

$Ru(bipy)_3$ considerably increases the rate of DMD decomposition. The dependence of the rate constant of chemiluminescence damping on the first part of the kinetic curve on $Ru(bipy)_3$ concentration is linear (see Figure 1): $k'_{cl} = a + b[Ru(bipy)_3]$, where a and b are constant values. From Figure 1 it follows that $a = (1.7\pm0.6)\times10^{-2}$, $b = (9.6\pm1.8)\times10^{3}$.

As we anticipated, the light total of the reaction in the system DMD_{abs}–silipor–$Ru(bipy)_3$ (see Figure 1), as well as chemiluminescence yield ($\approx 3\times10^{-7}$ Einstein mol^{-1}) is considerably higher then that on non-activated silipor. However, the yield of chemiexcitation of $Ru(bipy)_3$ ($\approx 3\times10^{-5}$) is one order of magnitude lower than the corresponding value for methyl acetate. Obviously, the increase in chemiluminescence in the presence of $Ru(bipy)_3$, adsorbed on silipor, is caused by the higher radiation yield of the complex (0.0095), which is three orders of magnitude higher than η_{rad} for methyl acetate.

One can suppose that the activation of luminescence by $Ru(bipy)_3$ in the course of the decomposition of DMD on the silipor proceeds *via* a chemically induced electron exchange luminescence mechanism (CIEEL), which is akin to that observed in solution:[6]



Taking into account the fact that dioxiranes possess a high enough electron affinity (2 eV)[18] and readily participate in electron-transfer reactions,[19] the CIEEL mechanism seems to be very possible.

It is of interest that the samples of silipor containing DPhA also give more intense chemiluminescence and accelerate the rate of DMD decomposition compared with that on the non-activated silipor. Thus, at 75 °C and [DPhA] = $= 1\times10^{-6}$ mol g^{-1} the rate constant observed and the maximum intensity of luminescence increase by 2 and 10 times, respectively. This was previously reported[1,20,21] for the oxidation of some polycyclic aromatic hydrocarbons (PAH) (such as chrysene, pyrene and others) adsorbed on a sorbent surface, by DMD. The main principle of the method was very close to that used by us in the present work, namely, DMD was supplied on a sorbent surface from the gas phase. Since DPhA is also related to PAH, it seems very possible that the interaction of the DMD_{abs} with the other PAH, adsorbed on the surface, will give us a very useful method for studying the kinetics of such reactions by following the chemiluminescence. However, this is the subject of further investigations.

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