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Formation of singlet oxygen in the system tris(bipyridine)ruthenium(II)–dimethyldioxirane

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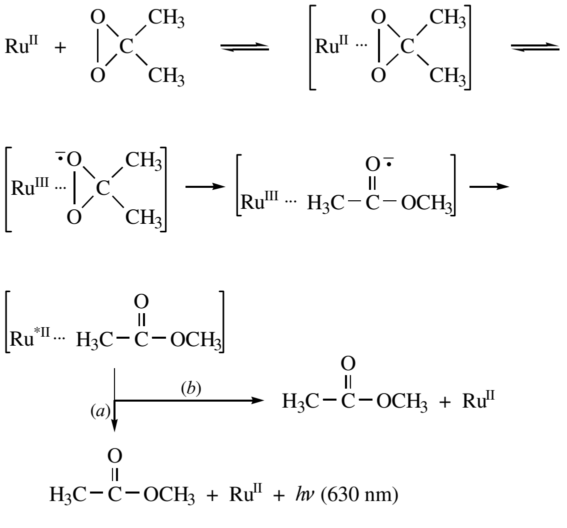
Decomposition of dimethyldioxirane in the presence of tris(bipyridine)ruthenium(II) complex (Ru^{II}) is accompanied by chemiluminescence (CL) in the infrared spectrum region (1270 nm) due to the formation of singlet oxygen; reaction between Ru^{III} and superoxide ion, which is formed in this process *via* a sequence of electron-transfer reactions, is assumed to be a CL step.

Dioxiranes are known to be powerful yet selective oxidizing reagents. These three-membered ring cyclic peroxides have become an intensively studied species over the last decade mainly owing to their role in oxygen-transfer reactions. Epoxidation of alkenes and oxygen insertion into the 'nonactivated' aliphatic C–H bonds of alkanes are prominent examples of these oxidations.[1–3] However, dioxiranes are also prone to electron-transfer (ET) reactions,[2,4–10] some of which are accompanied by chemiluminescence (CL).[2,7–10] Indeed, it is an ET mechanism, namely chemically induced electron exchange luminescence (CIEEL), that accounts for CL upon decomposition of methyl(trifluoromethyl)dioxirane (TFMD) and dimethyldioxirane (DMD) in the presence of some aromatic hydrocarbons.[2,7,10] The phenomenon of CL is a new and attractive property of dioxiranes which has begun to be explored only in recent years.

Recently, we reported on CL in the visible spectrum region (both in solution[9] and on a silipor surface[10]) in the Ru^{II}-promoted decomposition of DMD (CIEEL mechanism):



Scheme 1

In this communication we report that, besides the visible CL (Scheme 1), the interaction between DMD and catalytic amounts of Ru^{II} is also accompanied by CL in the infrared spectrum region (1270 nm) due to radiative deactivation of singlet oxygen.

The near infrared chemiluminescence of $^1O_2$ was recorded using apparatus described previously.[11] In a typical procedure, a solution of Ru^{II} in the appropriate solvent (1 ml, $[Ru^{II}]_0 = 1\times10^{-4}$ mol l^{-1}) was poured into a cell placed above the photocathode of a photomultiplier. Then, a DMD solution in acetone (0.5 ml, $[DMD]_0 = 5.25\times10^{-2}$ mol l^{-1}) was rapidly injected. All reactions were carried out at room temperature and under continuous argon flow. The apparatus for CL recording was calibrated using the emission from $^1O_2$ formed during thermal decomposition of triphenyl phosphite ozonide, using a known yield of singlet oxygen and decomposition rate.

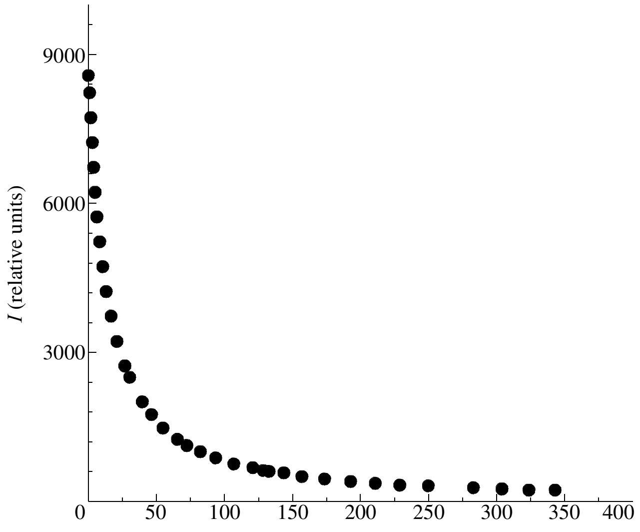


Figure 1 Typical kinetic curve for the singlet oxygen chemiluminescence decay in the system Ru^{II}–DMD. Starting conditions: solvent acetone–[$^2H_3$]acetonitrile (1:2), 25 °C, argon atmosphere, $[Ru^{II}]_0 = 6\times10^{-5}$ mol l^{-1}, $[DMD]_0 = 1.75\times10^{-2}$ mol l^{-1}.

The yield of $^1O_2$ formation per dioxirane molecule consumed was equal to 0.00084% (in acetone). The infrared CL at 1270 nm was solvent-dependent. Indeed, a significantly stronger signal was observed when the reaction was carried out in acetone–[$^2H_6$]acetone or acetone–[$^2H_3$]acetonitrile mixtures, which is in good agreement with the fact that in deuteriated solvents the lifetime of singlet oxygen is considerably higher than in non-deuteriated ones.[12] Thus, the yield of $^1O_2$ was equal to 0.0075% (in acetone–[$^2H_6$]acetone, 1:2) and 0.03% (in acetone–[$^2H_3$]acetonitrile, 1:2). However, the effect observed was much higher than that expected from the literature data on singlet oxygen life times (τ) in these deuteriated solvents.[12] Thus, the relative light sums were 1.0:13.9:56.0 in acetone, acetone–[$^2H_6$]acetone (1:2) and acetone–[$^2H_3$]acetonitrile (1:2), whereas the ratio of τ in these solvent mixtures[†] is 1.0:2.7:2.8. One can assume that apart from an increase in the radiative efficiency of $^1O_2$, an unexpectedly high isotope effect is associated with the interference of acetone or [$^2H_3$]acetonitrile during the process. It is likely that in the presence of [$^2H_6$]acetone or especially of [$^2H_3$]acetonitrile, where the isotope effect is even more pronounced, the reaction changes direction so that it favours more effective formation of singlet oxygen, which results in an additional increase in CL intensity. However, in order to establish exactly how this is occurring more experimental work needs to be done.

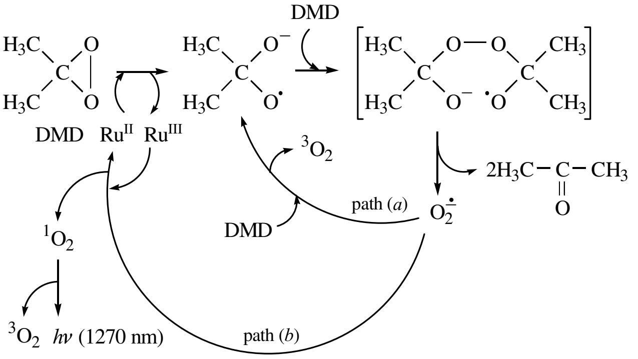
[†] Since the reactions were carried out in a mixture of deuteriated and non-deuteriated solvents, the τ values were estimated according to the Stern–Volmer equation taking into account the fact that the singlet oxygen lifetime is reduced upon adding acetone to [$^2H_6$]acetone or to [$^2H_3$]acetonitrile.

Luminescence decay follows a complex rate law and cannot be described with either first- or second-order kinetics (see Figure 1).

One possible path for singlet oxygen formation is the reaction between Ru^{III} and superoxide ion. In fact, it is known that $^1O_2$ is produced quantitatively in the Ru^{III}-superoxide reaction:[13]

$$\mathrm{Ru^{III}} + \mathrm{O_2^{\bullet -}} \longrightarrow {}^1\mathrm{O_2} + \mathrm{Ru^{II}}$$

Consequently, if these intermediates are really formed in our case, their interaction should lead to the generation of $^1O_2$. To explain the formation of Ru^{III}, superoxide and singlet oxygen, one can propose the following scheme for the process:



Scheme 2

Previously, Adam *et al.*[6] established a similar series of reactions [path (*a*)] for iodide ion-promoted decomposition of TFMD. In contrast to that case, we suggest here that another option available to the superoxide in our system is path (*b*), namely reaction with Ru^{III}, followed by the regeneration of the ruthenium to its initial oxidation state. It is this reaction that should lead to chemiluminescence of singlet oxygen in our system. It should be pointed out that this is already a secondary event when singlet oxygen is formed in the reactions of dioxiranes. It was previously reported on $^1O_2$ generation in the reaction of DMD with *N*-oxides, but in that case quite another mechanism operates.[14]

Thus, DMD, at least partially, participates in the ET process presented in Scheme 2 [paths (*a*) and (*b*)]. Perhaps this is one of the reasons [along with Ru^{II}-induced isomerization of DMD without formation of Ru*^{II}, Scheme 1, (*b*)] why the chemiexcitation yield of Ru^{II} in the CIEEL reaction [Scheme 1, (*a*)] was found to be rather small (0.01)[9] as compared with that in the case of 1,2-dioxetanes (0.2).[15,16]

One can suppose that interaction of the other transition metals with dioxiranes will also result in decomposition of the latter *via* the sequence of ET reactions presented in Scheme 2, and in some of these cases (if it is energetically allowed),[‡] the formation of singlet oxygen seems to be very possible. The observation of CL of $^1O_2$ in the system DMD–Ru^{II} opens a new and promising direction in the investigation of dioxirane properties and certainly awaits further experimentation.

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[‡] We failed to detect IR-CL under decomposition of DMD in the presence of Ce^{III} probably due to the high reduction potential of Ce^{IV}/Ce^{III} (1.4 V).[17] We were also unable to detect IR-CL during decomposition of DMD (adsorbed from the gas phase) on a silipor surface containing Ru^{II}. The diffusion limits, which inhibit the proceeding of the processes indicated in Scheme 2, seem to be responsible for this. However, the visible CL (Ru*^{II} emitter, 630 nm) according to CIEEL (Scheme 1) is observed under these conditions.[10]