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ScienceDirect
Mendeleev Commun., 2008, **18**, 249–250
Mendeleev Communications

A new bright chemiluminescent reaction: interaction of acetone with solid potassium peroxymonosulfate in the complex of europium nitrate

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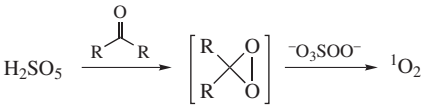
DOI: 10.1016/j.mencom.2008.09.006

The interaction of acetone with a mixture of potassium peroxymonosulfate and europium nitrate hexahydrate powders at 90 °C is accompanied by chemiluminescence due to the formation of excited Eu^{3+}; dioxirane is proposed to be a key intermediate responsible for the chemiluminescence observed.

Since 1974,[1] the ketone-catalyzed decomposition of peroxymonosulfuric acid (Caro's acid) in solution has attracted attention.[1–7] A reason for such a long-standing interest is that this reaction is a main synthetic route to dioxiranes,[3,4] highly efficient and selective oxidants, which are widely used (*in situ* or as an isolated solution) in oxidation chemistry.[8,9] Moreover, dioxiranes belong to a new class of hyperenergetic peroxides, which produce chemiluminescence (CL) during rearrangement to the corresponding esters[8] or oxidation of organic and inorganic substrates.[10,11] In particular, the study of the dioxirane CL has led to the discovery of a new mechanism of liquid-phase organic reactions, the so-called oxygen-transfer CL.[10]

Apart from dioxirane involvement, the Caro's acid–acetone system is a highly efficient source of singlet excited oxygen ($^1O_2$),[5] whose importance in environmental and biomedical sciences, chemi- and bioluminescence, as well as in organic synthesis, is now well recognized.[12–14] Note that it is the reaction of intermediate dioxirane with the monopersulfate ion that leads to the formation of $^1O_2$ (Scheme 1).



Scheme 1

Thus, the study of excited states generation in the acetone-catalyzed decomposition of peroxymonosulfuric acid could provide promising interdisciplinary perspectives. But the CL observed in visible spectral region in the reaction of HSO_5^- with acetone in aqueous solution is only very weak (so-called extra weak CL) with a CL yield of as low as 10^{-11} einstein mol^{-1} even in the presence of the CL activator europium nitrate. However, we discovered that a simple change of reaction conditions, namely, going from the liquid to the solid phase, results in a drastic increase in the CL efficiency by several orders of magnitude, so that under appropriate conditions in the presence of $Eu(NO_3)_3$ luminescence may be observed in a slightly darkened room even by naked eye.

After the rapid (~1 s) injection of 0.3 ml of liquid acetone to a cuvette containing a finely pounded mixture of 20 mg of Oxone (5.8×10^{-5} mol of $KHSO_5$) and 17 mg of $Eu(NO_3)_3$ (3.8×10^{-5} mol) powders, preheated for 5 min at 90 °C, a strong luminescence signal was observed.† The CL reached its maximum intensity after 5 min and then slowly decayed to zero in about 5.6 h at 90 °C. During that time, 4.5×10^{-5} mol of $KHSO_5$ was consumed, as revealed by iodometric analysis of the reaction mixture.

Notably, when the interaction of acetone with powders was carried out at higher temperature (200 °C) and with 50 mg of each Oxone and $Eu(NO_3)_3$ rather bright red emission could be observed even by naked eye in a slightly darkened room (see Online Supplementary Materials). The red colour of the CL is caused by the emission of Eu^{3+}, as shown by the high-temperature solid phase CL spectrum (Figure 1) with a double maximum at 614 and 628 nm, which correlates well with the emission maximum of europium photoluminescence between 610 and 630 nm.[15]

The maximum intensity of CL and the total amount of light evolved in the reaction at 90 °C were determined by actinometry to $I_{CL} = 1.7\times10^{-15}$ einstein s^{-1} and $S = 4.3\times10^{-12}$ einstein, respectively. These data allow us to calculate the CL yield of $\eta_{CL} = 1.0\times10^{-7}$ einstein mol^{-1} (based on the consumed peroxide).

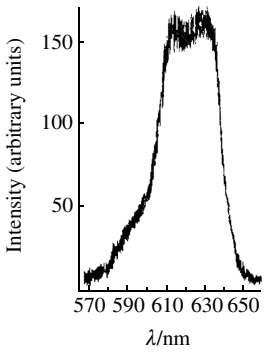
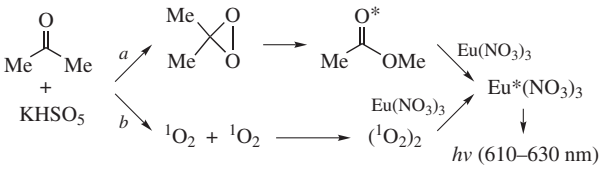


Figure 1 Chemiluminescence spectrum taken during the reaction of 0.1 ml of acetone with a solid mixture of 20 mg of Oxone and 17 mg of $Eu(NO_3)_3$ at 90 °C.

† CL measurements were performed at 90 °C with a photomultiplier sensitive between 330 and 800 nm. The source of $KHSO_5$ was the triple salt $2KHSO_5\times KHSO_4\times K_2SO_4$ (Oxone, Aldrich). Acetone was distilled before use. Europium nitrate $Eu(NO_3)_3\cdot6H_2O$ (Aldrich) was recrystallized from twice-distilled water. The dimethyldioxirane solution in acetone was prepared as described in the literature.[3,4]

Because the reaction temperature of 90 °C is much higher than the boiling point of acetone (56 °C), the ketone was immediately evaporated after addition to the mixture of Oxone and $Eu(NO_3)_3$ powders. Therefore, it is obvious that the overall CL, lasting for several hours, is caused by the interaction of $Eu(NO_3)_3/KHSO_5$ with acetone vapour rather than liquid acetone.‡ The following experiment was conducted to confirm this assumption: 3 ml of acetone was transferred to a room temperature cuvette, which was connected by a tube with a second cuvette placed above the photocathode of the photomultiplier and containing the mixture of 20 mg of Oxone and 17 mg of $Eu(NO_3)_3$ powders. This cuvette was thermostatted at 90 °C for 5 min; then, a gentle argon flow entered the first cuvette, captured the acetone vapour and entered the second one with the powder mixture. A rise of the CL signal was instantly observed, which reached its maximum after 20 min and decayed during 7 h at 90 °C. Chemiluminescent characteristics were comparable with those obtained with the above injection experiment: $I_{CL} = 1.7\times10^{-15}$ einstein s^{-1}, $S = 6.7\times10^{-12}$ einstein and $\eta_{CL} = 2.0\times10^{-7}$ einstein mol^{-1}.



Scheme 2

We propose that the excitation of Eu^{3+} occurs *via* the involvement of intermediate dioxirane as shown in Scheme 2 (pathway *a*): the rearrangement of dimethyldioxirane may lead to the excited methyl acetate[8] followed by energy transfer to the europium ion. Indeed, we have found that interaction of the vapour of isolated dimethyldioxirane[3,4] with 17 mg of pure $Eu(NO_3)_3$ powder at 90 °C is accompanied by CL whose efficiency was found with $S = 1.1\times10^{-11}$ einstein to be even higher than that obtained in the acetone–$KHSO_5$–$Eu(NO_3)_3$ system. The yield of CL, based on the amount of spent dioxirane, was 2.2×10^{-7} einstein mol^{-1}. This result strongly supports the proposed mechanism.

Furthermore, NMR analysis of the crude reaction mixture, taken after the CL reaction of the injection experiment with $KHSO_5$–$Eu(NO_3)_3$ powders was completed, revealed the presence of acetone.§ Apart from the acetone signal and several unidentified signals, the NMR displayed also signals which could be attributed to the methyl acetate, a product of dimethyldioxirane rearrangement. This observation lends further support to the proposed pathway *a* of Scheme 2. It seems very likely that methyl acetate and acetone have not been evaporated at 90 °C because they were bound in a complex with europium so that interaction of acetone with $KHSO_5$ takes place in the metal coordination sphere.

However, considering the involvement of intermediate dioxirane, we cannot exclude alternative pathway *b* in Scheme 2, in which europium nitrate may be excited by energy transfer from the singlet-oxygen dimol species $(^1O_2)_2$, which are known to be formed during the acetone-catalyzed decomposition of $KHSO_5$ in solution.[13,16] The possibility of energy transfer from $(^1O_2)_2$ to appropriate fluorescers has been postulated[17] in 1966 and has later often been invoked to explain light emission in several chemi- and photoluminescent reactions.[13]

In conclusion, we found that the interaction of acetone vapour with solid potassium peroxymonosulfate leads, in the presence of europium nitrate, to bright CL, which may be observed even by naked eyes in a slightly darkened room. We propose that dioxirane or/and singlet-oxygen dimol are key intermediates, which are responsible for the excitation of the europium complex. To the best of our knowledge, CL in the reaction of ketone with solid-phase $KHSO_5$ is unprecedented.

This work was supported by the Russian Foundation for Basic Research (grant no. 08-03-00147-a), the Leading Scientific School Support Program (NSh-2206.2008.3), the Branch of Chemistry and Material Sciences of the Russian Academy of Sciences (no.1-OKh), and a programme of the Ministry of Education and Science of the Russian Federation (RNP 2.2.1.1.6332). R.S. aknowledges the support of Adolf-Messer-Stiftung.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2008.09.006.

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Received: 17th April 2008; Com. 08/3124

‡ Interaction between $Eu(NO_3)_3$ and $KHSO_5$ as a source of CL may be exluded since in a separate experiment we have shown that the total amount of light evolved in this reaction (*i.e*., in the absence of acetone) was as low as 2–3% of that in the $Eu(NO_3)_3$–$KHSO_5$–acetone system.

§ The identification of reaction products was carried out under conditions analogous to those where CL measurements have been performed. 0.3 ml of liquid acetone was rapidly injected into the cuvette (the total volume of the cuvette was 14 ml) containing a mixture of Oxone and $Eu(NO_3)_3\cdot6H_2O$ powders, which was preheated for 5 min at 90 °C. Then, the cuvette with powders was thermostated at 90 °C during 6 h (a time which corresponds to the end of CL reaction). After that, the crude reaction mixture was allowed to cool down to room temperature, diluted with 4 ml of H_2O and extracted with 1 ml of $CDCl_3$ with subsequent analyses by ^1H and ^{13}C NMR spectroscopy. Alternatively, the reaction mixture was diluted with 1.3 ml of D_2O and an aliquot portion was directly analyzed by NMR spectroscopy (Bruker AM-300) in this solvent. NMR spectra contained characteristic signals of acetone in D_2O: ^1H NMR, δ: 2.08 (s, Me); ^{13}C NMR, δ: 30.03 (Me), 203.69 (C=O); in $CDCl_3$: ^1H NMR, δ: 2.13 (s, Me); ^{13}C NMR, δ: 30.87 (Me), 207.01 (C=O). Likewise, methyl acetate was characterized by the following signals in D_2O: ^1H NMR, δ: 2.15 (s, Me), 3.73 (s, OMe); ^{13}C NMR, δ: 50.22 (OMe), 175.22 (O–C=O), 19 (Me); in $CDCl_3$: ^1H NMR, δ: 2.03 (s, Me), 3.63 (s, OMe); ^{13}C NMR, δ: 60.36 (OMe), 185.14 (O–C=O), 20.99 (Me).