

A new bright chemiluminescent reaction: interaction of acetone with solid-phase potassium monoperoxy sulfate in the complex of europium nitrate

Dmitri V. Kazakov,^{*a} Farit E. Safarov,^b Valeri P. Kazakov^a

⁵ *Receipt/Acceptance Data*

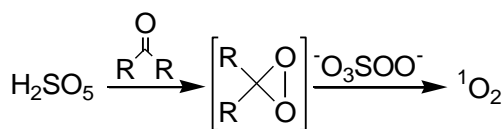
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Interaction of the acetone with a mixture of potassium monoperoxy sulfate and europium nitrate hexahydrate powders at 90 °C is accompanied by chemiluminescence (CL) due to formation of the excited Eu³⁺; dioxirane is proposed to be a key intermediate responsible for the CL observed.

Since the first report in 1974,¹ the ketone-catalyzed decomposition of monoperoxy sulfuric acid (Caro's acid) in solution has attracted attention of many research groups.² One of the reasons for such a long-standing interest is that this reaction is a main synthetic route to dioxiranes,³ highly efficient and selective oxidants, which are widely used (in situ or as an isolated solution) in oxidation chemistry.^{2a-d,g-k,3} Moreover, dioxiranes appeared to be a new class of hyperenergetic peroxides which produce chemiluminescence (CL) during rearrangement to the corresponding esters^{3b,c,4d,e} or oxidation of organic and inorganic substrates.^{4a-c} 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.^{4a} It is also most remarkable that dioxiranes not only play an important role in CL but also have been proposed to be involved as intermediates in biochemical processes,⁵ in particular the ones that lead to bioluminescence.^{5b,c}

Apart from dioxirane involvement, the Caro's acid/acetone system is a highly efficient source of singlet excited oxygen (¹O₂),^{2e,f,6} whose importance in environmental and biomedical sciences, chemi- and bioluminescence as well as in organic synthesis is now well recognized.⁷ Notably it is the reaction of intermediary dioxirane with monoperoxy sulfate ion that leads to the formation of ¹O₂ (Scheme 1).



Scheme 1

Thus, the study of excited states generation in the acetone-catalyzed decomposition of monoperoxy sulfuric acid could provide promising interdisciplinary perspectives. But the CL observed in visible spectral region in the reaction of HSO₅⁻ with acetone in aqueous solution is only very weak (so-called extra weak CL) with a CL yield as low as 10⁻¹¹ Einstein mol⁻¹ even in the presence of the chemiluminescence activator europium nitrate. However, we discovered that a simple change of the reaction conditions, namely going from the liquid to the solid phase, results in a drastic increase

of the CL efficiency by several orders of magnitude, such that under appropriate conditions in the presence of Eu(NO₃)₃ the luminescence may be observed in a slightly darkened room even by naked eye.

After rapid (*ca.* 1 s) injection of 0.3 ml of liquid acetone to a cuvette containing a finely pounded mixture of 20 mg Curox (= 5.8×10⁻⁵ mol of KHSO₅) and 17 mg Eu(NO₃)₃ (= 3.8×10⁻⁵ mol) powders, preheated for 5 minutes at 90 °C, the appearance of a strong luminescence signal was observed.[†] The CL reached its maximum intensity after five minutes and decayed then slowly to zero in about 5.6 hours at 90 °C. During that time 4.5×10⁻⁵ mol of KHSO₅ have been 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 Curox and Eu(NO₃)₃ rather bright red emission could be observed even by naked eye in slightly darkened room (see Supp. Inf.). The red color of the CL is caused by the emission of Eu³⁺, as shown by the high temperature solid phase CL spectrum of Figure 1 with its double maximum at 614 and 628 nm which correlates well with emission maximum of the europium photoluminescence between 610 and 630 nm.⁸

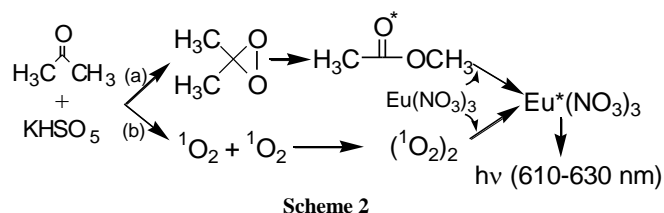
The maximum intensity of CL and the total amount of light evolved in the reaction at 90 °C were determined by actinometry to I_{CL} = 1.7×10⁻¹⁵ Einstein s⁻¹ and S = 4.3×10⁻¹² Einstein, respectively. These data allow the calculation of the CL yield to η_{CL} = 1.0×10⁻⁷ Einstein mol⁻¹ (based on the consumed peroxide).

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 Curox and Eu(NO₃)₃ powders. It is therefore obvious that the overall CL, lasting for several hours, is caused by the interaction of Eu(NO₃)₃/KHSO₅ with vaporous but not with liquid acetone. The following experiment was conducted to confirm this assumption. 3 ml acetone have been 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 Curox and 17 mg Eu(NO₃)₃ powders. This cuvette was thermostatted at 90 °C for 5 minutes, and then a gentle argon flow entering the first cuvette captured the acetone vapor 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 seven hours at 90 °C. Chemiluminescent characteristics were found to be comparable with those obtained with the above described injection experiment: I_{CL} = 1.7×10⁻¹⁵ Einstein s⁻¹, S = 6.7×10⁻¹² Einstein, η_{CL} = 2.0×10⁻⁷ Einstein mol⁻¹.



Fig. 1 Chemiluminescence spectrum taken during the reaction of 0.1 ml acetone with a solid mixture of 20 mg Curox and 17 mg $\text{Eu}(\text{NO}_3)_3$ at 90 °C.

We propose that excitation of Eu^{3+} occurs via involvement of the intermediary dioxirane as shown in Scheme 2 (pathway *a*): Rearrangement of the dimethyldioxirane may lead to the excited



methylacetate^{3b,c,4d,e} followed by energy transfer to the europium ion. Indeed, we have found that interaction of the vapor of isolated dimethyldioxirane³ with 17 mg pure $\text{Eu}(\text{NO}_3)_3$ powder at 90 °C is accompanied by CL whose efficiency was found with $S = 1.1 \times 10^{-11}$ Einstein to be even higher than that obtained in acetone/ $\text{KHSO}_5/\text{Eu}(\text{NO}_3)_3$ system. The yield of CL, based on amount of the 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 $\text{KHSO}_5/\text{Eu}(\text{NO}_3)_3$ powders was completed, revealed the presence of acetone.[‡] Apart from the acetone signal and a 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. Obviously, methylacetate 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 involvement of the intermediary dioxirane we cannot exclude the alternative pathway *b* of Scheme 2, in which europium nitrate may be excited by energy transfer from the singlet-oxygen dimol species ($^1\text{O}_2$)₂, which are known to be formed during the acetone-catalyzed decomposition of KHSO_5 in solution.⁹ The possibility of energy transfer from ($^1\text{O}_2$)₂ to appropriate fluorescers has been postulated¹⁰ already in 1966 and has later often been invoked to explain light emission in several chemi- and photoluminescent reactions.^{7a}

In conclusion, we have shown that interaction of acetone vapor with solid phase potassium peroxydisulfate leads in the presence of europium nitrate to a bright chemiluminescence 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.

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Notes and references

† Chemiluminescence measurements have been performed at 90 °C with a photomultiplier sensitive between 330 and 800 nm. The source of the KHSO_5 was the triple salt $2\text{KHSO}_5 \times \text{KHSO}_4 \times \text{K}_2\text{SO}_4$ (Curox), which was used as received. Acetone (p.a.) was distilled prior to use. Europium nitrate $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Aldrich) was recrystallized from twice distilled water. Dimethyldioxirane solution in acetone has been prepared as described in the literature.^{2c,3e,f}

‡ Identification of the reaction products has been carried out as follows. After the CL reaction was completed, the crude reaction mixture was diluted in H_2O and extracted by CDCl_3 with subsequent analyses by ^1H - and ^{13}C -NMR spectroscopy. Alternatively, reaction mixture was diluted in D_2O and directly analyzed by NMR spectroscopy (Bruker AM-300) in this solvent. NMR spectra contain characteristic signals of acetone in D_2O : ^1H NMR δ 2.08 (s, CH_3), ^{13}C NMR δ 30.03 (CH_3), 203.69 (C=O); in CDCl_3 : ^1H NMR δ 2.13 (s, CH_3), ^{13}C NMR δ 30.87 (CH_3), 207.01 (C=O). Likewise, methylacetate was characterized by the following signals: D_2O : ^1H NMR δ 2.15 (s, CH_3), 3.73 (s, OCH_3), ^{13}C NMR δ 50.22 (OCH_3), 175.22 (O-C=O), 19 (CH_3); in CDCl_3 : ^1H NMR δ 2.03 (s, CH_3), 3.63 (s, OCH_3), ^{13}C NMR δ 60.36 (OCH_3), 185.14 (O-C=O), 20.99 (CH_3).

§ Preliminary results from the luminescent-kinetics studies further support proposition that the reaction occurs in the europium coordination sphere. Investigations on the precise mechanism of the process are currently in the progress.

- R.E. Montgomery, *J. Am. Chem. Soc.*, 1974, **96**, 7820.
- (a) J.O. Edwards, R.H. Pater, R. Curci and F. Di Furia, *Photochem. Photobiol.*, 1979, **30**, 63; (b) R. Curci, M. Fiorentino and M.R. Serio, *J. Chem. Soc., Chem. Commun.*, 1984, 155; (c) R.W. Murray and R. Jeyaraman, *J. Org. Chem.*, **1985**, *50*, 2847; (d) A. Armstrong, P.A. Clarke and A. Wood, *J. Chem. Soc., Chem. Commun.*, 1996, 849; (e) A. Lange and H.-D. Brauer, *J. Chem. Soc., Perkin Trans. 2*, 1996, 805; (f) A. Lange, M. Hild and H.-D. Brauer, *J. Chem. Soc., Perkin Trans. 2*, 1999, 1343; (g) H.Q. Thian, X.G. She, J.X. Xu and Y. Shi, *Org. Lett.*, 2001, **3**, 1929; (h) S.E. Denmark and H. Matsuhashi, *J.*

- Org. Chem.*, 2002, **67**, 3479; (i) Y. Shi, *Acc. Chem. Res.*, 2004, **37**, 488; (j) D. Yang, *Acc. Chem. Res.*, 2004, **37**, 497; (k) A. Armstrong and T. Tsuchiya, *Tetrahedron*, 2006, **62**, 257.
- 3 (a) W. Adam, C.R. Saha-Müller and C.-G. Zhao, *Org. React.*, 2002, **61**, 219; (b) V.P. Kazakov, A.I. Voloshin and D.V. Kazakov, *Russ. Chem. Rev.*, 1999, **68**, 253; (c) W. Adam, R. Curci and J.O. Edwards, *Acc. Chem. Res.*, 1989, **22**, 205; (d) R.W. Murray, *Chem. Rev.*, 1989, **89**, 1187; (e) W. Adam, Y.Y. Chan, D. Cremer, J. Gauss, D. Scheutzow and M. Schindler, *J. Org. Chem.*, 1987, **52**, 2800; (f) W. Adam, J. Bialas and L. Hadjiarapoglou, *Chem. Ber.*, 1991, **124**, 2377.
- 4 (a) D.V. Kazakov, A.B. Barzilova and V.P. Kazakov, *Chem. Commun.*, 2001, 191; (b) D.V. Kazakov, G.Ya. Maistrenko, N.P. Polyakova, R.R. Latypova, V.P. Kazakov, W. Adam, A.V. Trofimov, C.-G. Zhao, W. Kiefer and S. Schlücker, *Luminescence*, 2002, **17**, 293; (c) W. Adam, D.V. Kazakov, V.P. Kazakov, W. Kiefer, R.R. Latypova and S. Schlücker, *Photochem. Photobiol. Sci.*, 2004, **3**, 182; (d) D.V. Kazakov, N.N. Kabalnova, A.I. Voloshin, V.V. Shereshovets and V.P. Kazakov, *Russ. Chem. Bull.*, 1995, **44**, 2193; (e) W. Adam and R. Curci, *Chim. Ind. (Milan)*, 1981, **63**, 20.
- 5 (a) R. Mello, M. Fiorentino, C. Fusco and R. Curci, *J. Am. Chem. Soc.*, 1989, **111**, 6749; (b) F.M. Raushel and T.O. Baldwin, *Biochem. Biophys. Res. Commun.*, 1989, **164**, 1137; (c) W.A. Francisco, H.M. Abu-Soud, A.J. DelMonte, D.A. Singleton, T.O. Baldwin and F.M. Raushel, *Biochemistry*, 1998, **37**, 2596.
- 6 D.F. Evans and M.W. Upton, *J. Chem. Soc., Dalton Trans.*, 1985, 1151.
- 200 7 (a) W. Adam, D.V. Kazakov and V.P. Kazakov, *Chem. Rev.*, 2005, **105**, 3371; (b) C. Schweitzer and R. Schmidt, *Chem. Rev.*, 2003, **103**, 1685; (c) J.-M. Aubry, C. Pierlot, J. Rigaudy and R. Schmidt, *Acc. Chem. Res.* 2003, **36**, 668; (d) W. Adam and M. Prein, *Acc. Chem. Res.*, 1996, **29**, 275; (e) *Singlet Oxygen*, Frimer, A.A. Ed., CRC: Boca Raton, Florida, 1985; (f) A.A. Krasnovsky, Jr. *Biofizika*, 2004, **49**, 305; (g) F. Wilkinson, *Pure Appl. Chem.*, 1997, **69**, 851; (h) R. Schmidt, *Photochem. Photobiol.*, 2006, **82**, 1161; (i) R. W. Redmond and I. E. Kochevar, *Photochem. Photobiol.*, 2006, **82**, 1178; (j) E. Skovsen, J. W. Snyder and P. R. Ogilby, *Photochem. Photobiol.*, 2006, **82**, 1187; (k) M. T. Jarvi, M. J. Niedre, M.S. Patterson and B.C. Wilson, *Photochem. Photobiol.*, 2006, **82**, 1198; (l) É. Hideg, T. Kálai, P. B. Kós, K. Asada and K. Hideg, *Photochem. Photobiol.*, 2006, **82**, 1211; (m) J. Cadet, J.-L. Ravanat, G. R. Martinez, M. H. G. Medeiros and P. Di Mascio, *Photochem. Photobiol.*, 2006, **82**, 1219.
- 210 8 (a) E. Moret, J.-C. G. Bunzli and K.J. Schenk, *Inorg. Chim. Acta*, 1990, **178**, 83; (b) M.J. Lochhead, P.R. Wamsley and K.L. Bray, *Inorg. Chem.*, 1994, **33**, 2000; (c) G. Blasse, G.J. Dirksen and J.P.M. Van Vliet, *Inorg. Chim. Acta*, 1988, **142**, 165.
- 220 9 W. Adam, V.P. Kazakov, D.V. Kazakov, R.R. Latypova, G.Ya. Maistrenko, D.V. Mal'zev, F.E. Safarov, In *Bioluminescence & Chemiluminescence: Progress and Perspectives*; Tsuji, A.; Matsumoto M.; Maeda, M.; Kricka, L.J.; Stanley, P.E., Eds.; World Scientific, Singapore, 2005, p. 135-138.
- 225 10 A.U. Khan and M. Kasha, *J. Am. Chem. Soc.*, 1966, **88**, 1574.

^a Institute of Organic Chemistry, Ufa Scientific Center of the RAS, 71 Pr. Oktyabrya, 450054 Ufa, Russia. Fax: +7 3472 356066; Tel: +7 3472 356111; E-mail: chemlum@ufanet.ru

^b Department of Chemistry, Bashkir State University, 32 Ul. Frunze, 450007 Ufa, Russia.

^c Institut für Physikalische und Theoretische Chemie, Johann Wolfgang Goethe-Universität Frankfurt, Max-von-Laue-Strasse 7, D-60438 Frankfurt am Main, Germany. Fax: +49 069 798 29448; Tel: +49 069 798 29445; E-mail: R.Schmidt@chemie.uni-frankfurt.de

† Electronic Supplementary Information (ESI) available: [Photograph of the CL taken during the reaction of acetone with a solid mixture of Curox and Eu(NO₃)₃·6H₂O]. See <http://dx.doi.org/10.1039/b000000x/>

Abstract for the contents pages

A bright chemiluminescence is observed during the interaction of the acetone (liquid or vapor) with a mixture of potassium monoperoxysulfate and europium nitrate hexahydrate powders at 90 °C. The light is emitted by an excited Eu^{3+} . Dioxirane is proposed to be a key intermediate responsible for the europium excitation.

