

A novel chemiluminescence from the reaction of dioxiranes with alkanes. Proposed mechanism of oxygen-transfer chemiluminescence

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Oxidation of adamantane and 2,3-dimethylbutane by methyl(trifluoromethyl)dioxirane is accompanied by chemiluminescence (CL); formation of the emitter of CL, triplet excited trifluoropropanone, is proposed to occur *via* a concerted oxenoid mechanism of oxygen insertion into C–H bond of the hydrocarbons.

Chemiluminescence (CL) is a promising rapidly developing area of chemistry of new class of hyperenergetic molecules—dioxiranes.^{1,2,3a,b,4} In 1981 it was suggested¹ that isomerization of dioxirane into the corresponding ester should lead to the electronic excitation of the latter. Recently it was revealed that decomposition of dioxiranes in the absence of reactive substrates under certain conditions really results in production of the light emission.^{2,3a,b} Apart from the study of CL of isolated dioxiranes, dioxirane intermediate has been also postulated to explain luminescence in biochemical systems.⁵

On the other hand, dioxiranes are known to be highly effective yet selective oxidants in respect to various classes of organic compounds.³ Some of these oxidation reactions are exothermic enough⁶ to generate excited species and consequently to produce CL. The area of oxidative CL of dioxiranes seems to be highly perspective from the viewpoint of fundamental questions of chemistry of excited states since it could provide new valuable information not only on mechanisms of CL, but also on some aspects of generation of light in biochemical reactions as it has been suggested that dioxirane intermediates may be involved in biochemical oxidations.^{7a} However, in spite of these promising perspectives, so far the literature contained only a single report on generation of CL in the course of oxidative reactions of isolated dioxiranes. In 1994 CL occurring during oxidation of olefin (9-arylmethylene-10-methyl-9,10-dihydroacridine) with isolated dimethyldioxirane (DMD) was reported.⁴

In this communication we report the observation of a novel type of CL of dioxiranes occurring during oxidation of saturated hydrocarbons, such as adamantane (Ad) and 2,3-dimethylbutane (DMB), with isolated methyl(trifluoromethyl)dioxirane (TFD).^{7a} We also suggest a plausible mechanism of luminescence generation. To the best of our knowledge, CL in the reaction of alkanes with dioxiranes is unprecedented.

We have found that interaction of Ad and TFD is accompanied by light emission in the visible spectrum region ($\lambda_{\max} = 430\text{--}470$ nm). Under air atmosphere, the maximum intensity of CL and the total amount of light (S) evolved in the reaction (18 °C, CCl_4 , $[\text{Ad}]_0 = 0.063$ mol l⁻¹, $[\text{TFD}]_0 = 0.0019$ mol l⁻¹) were equal to 2×10^6 photon s⁻¹ml⁻¹ and 1.4×10^7 photon ml⁻¹ respectively. However, significant increase in CL intensity (I_{CL}) was observed when the reaction was carried out under nitrogen atmosphere. This effect testifies in favour of the triplet nature of the CL emitter since it is known that oxygen quenches triplet excited states.

Reaction of Ad with TFD is known^{7a,b} to obey a second order low (first order on each substrate):

$$W = k_2[\text{Ad}][\text{TFD}]$$

or, under pseudo-first order conditions:

$$W = k_1[\text{TFD}], \text{ where } k_1 = k_2[\text{Ad}].$$

Indeed, under $[\text{TFD}]_0 \ll [\text{Ad}]_0$, the plots $\ln(I_{\text{CL}})$ vs. time were found to be linear, yielding reproducible values of k_1 . From this k_2 values were estimated at different temperatures (Table 1). The activation parameters for k_2 calculated from the data of Table 1 are equal to $E_a = 8.2 \pm 0.7$ kcal mol⁻¹ and $\log A = 6.5 \pm 0.5$.

Under pseudo-first order conditions the rate of the reaction (W) is connected with the CL intensity by the following expression:

$$I_{\text{CL}} = \varphi_{\text{CL}} W = \varphi_{\text{CL}} k_2 [\text{Ad}][\text{TFD}] = k_1 [\text{TFD}] \quad (1)$$

where φ_{CL} is yield of CL.

The value of φ_{CL} was estimated from eqn. (1) using k_2 values taken from Table 1. Thus, at 18 °C φ_{CL} is equal to 1.2×10^{-11} Einstein mol⁻¹. The yield of CL calculated from the ratio $S/[\text{TFD}]_0 \approx 1.16 \times 10^{-11}$ Einstein mol⁻¹ is in agreement with that obtained from eqn. (1).

CL occurring under interaction of dioxiranes with alkanes appeared to be a more general phenomenon. In fact, we have found that interaction of DMB with TFD is also accompanied by light emission. The yield of CL (estimated as $S/[\text{TFD}]_0$ ratio) is equal to 2.6×10^{-12} Einstein mol⁻¹ (at 18 °C). It is important to note that the region of CL appeared to be the same as for the reaction of TFD with AD, *i.e.* $\lambda_{\max} = 430\text{--}470$ nm.

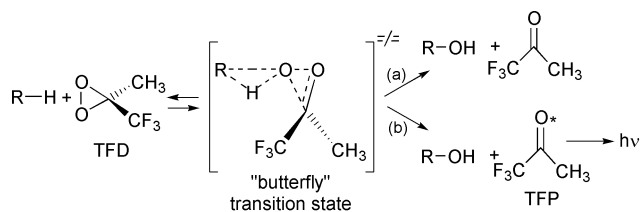
What is the mechanism of CL occurring under reaction of TFD with Ad and DMB? Interaction of alkanes with dioxiranes is known^{3,7} to result in the formation of the corresponding alcohol and ketone–dioxirane reduction product. In the course of previous studies it was shown^{3,7} that oxidation of alkanes (including Ad and DMB) by TFD is a bimolecular reaction implying involvement of high-ordered (so-called butterfly) transition state (Scheme 1 (path (a))).[†]

Therefore, it seems to be reasonable to attribute the light emission to the mechanism depicted in Scheme 1. According to the proposed mechanism only corresponding alcohol R–OH and trifluoropropanone (TFP) could be regarded as potential CL emitters. However, we can exclude alcohols from the consideration since they emit in the shorter wavelength region of spectrum than that recorded for CL in our system. Indeed, the range of CL observed upon oxidation of DMB and AD by TFD corresponds to the phosphorescence (PS) of TFP, testifying that

Table 1 Dependence of the rate constant of oxidation of Ad by TFD on temperature (solvent- CCl_4 , N_2 atmosphere^a)

T/K	251	262	272	279.5	283.5	288.5	291.5
k_2 (l mol ⁻¹ s ⁻¹)	0.23 ^c	0.47	0.73	1.42	1.57	1.83	2.25
	0.51 ^b						

^a Estimated as $k_2 = (k_1/[\text{Ad}]_0)$; k_1 values were obtained from pseudo-first order kinetic plots of CL damping with $[\text{TFD}]_0 = 1.8\text{--}3.8 \times 10^{-3}$ mol L⁻¹ and $[\text{Ad}]_0 = 4\text{--}6.3 \times 10^{-2}$ mol L⁻¹; most data are averages ($\pm 5\%$) from duplicate or more runs. ^b Value of the rate constant obtained previously^{7a} (in CH_2Cl_2 –TFP mixture) under second-order rate conditions by non-CL method (GLC). ^c Extrapolated to 251 K from Arrhenius equation. ^d Replacing N_2 with O_2 atmosphere does not affect the rate constant of the reaction.



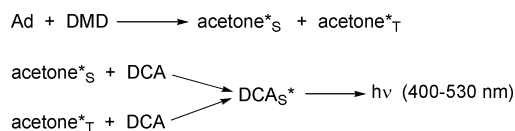
where R-H - adamantane or 2,3-dimethylbutane

Scheme 1

the latter in triplet excited state (TFP^*_T) is indeed an emitter of CL. Recent calculations^{5a} also favor the proposed mechanism of CL: oxygen insertion into C–H bonds of saturated hydrocarbons was shown to be about -65 – -70 kcal mol⁻¹ exothermic^{6a} so that the sum of enthalpy and activation energy (according to our data *ca.* 8 kcal mol⁻¹ for the reaction of Ad with TFD) should be sufficient for excitation (Scheme 1, path (b)) of, at least, triplet state of TFP. In fact, the energetic level of TFP^*_T is equal⁸ to *ca.* 75 kcal mol⁻¹, whereas the singlet excited level of TFP^*_S is about 9 kcal mol⁻¹ higher and unlikely to be occupied in the reaction.

One may note that the yield of CL arising during oxidation of alkanes with TFD was found to be relatively low. This fact is not surprising since numerous oxidation reactions are characterized by rather low yields of CL (ultra-weak CL). In particular, this is characteristic for light emission recorded in certain biological systems.⁹

It is of interest that we failed to record CL upon interaction of Ad with less reactive DMD. This is despite the fact that DMD, similar to TFD, is known to oxidize Ad into the corresponding alcohol.^{7e} Probably, the slower rate of Ad oxidation by DMD, compared with that of TFD,^{7b} accounts for the impossibility of recording CL due to its low intensity and the quenching of excited acetone (formed by analogy with TFP) by molecules of solvents or other reagents. However, introduction of 9,10-dicyanoanthracene (DCA) in the system results in the appearance of light emission ($[\text{DMD}]_0 = 3.1 \times 10^{-2}$ mol l⁻¹, $[\text{Ad}]_0 = 4 \times 10^{-2}$ mol l⁻¹, $[\text{DCA}]_0 = 6.6 \times 10^{-5}$ mol l⁻¹, CCl_4 -acetone = 2:1, 20 °C). DCA was found to be the emitter of the CL observed. One may suppose, that in this case DCA serves as a CL activator and enhances CL intensity as a result of energy transfer from excited acetone, formed by analogy with the mechanism suggested for TFD oxidation of alkanes (Scheme 1, path (b)). However, in contrast to the TFD case, along with triplet ketone, significant contribution of singlet excited states of acetone seems to have taken place since only insignificant quenching (*ca.* 20%) of CL intensity by oxygen is observed in this reaction. Consequently, excitation of DCA is likely to be caused by transfer of energy from both singlet and triplet excited molecules of acetone (Scheme 2).



Scheme 2

Likewise, effect of CL enhancement is observed when reaction of TFD and AD is carried out in the presence of DCA, obviously due to transfer of energy from the TFP^*_T on the activator with subsequent radiative deactivation of the latter.

In conclusion, oxidation of alkanes by TFD is accompanied by CL. We have proposed a plausible mechanism of CL (Scheme 1 (path b)) to explain our observations. We suggest to call this novel type of CL *butterfly chemiluminescence* or, in more general sense, *oxygen-transfer chemiluminescence*. To the best of our knowledge, this is a new mode of chemiexcitation not only for dioxiranes but also for other liquid-phase organic reactions with peroxide participation.

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Notes and references

† Oxidation of DMB by TFD (as 1:1 ratio) leads exclusively to the corresponding alcohol.^{7a} Likewise, interaction of Ad and TFD (as 0.9 ratio) results in the formation of 94% of adamantan-1-ol (Ad-OH), 5% of adamantane-1,3-diol and trace amounts of adamantanone (as a result of further oxidation of Ad-OH).^{7b} Apart from these compounds and TFP no other products or even intermediates were detected in the course of the reactions of alkanes with TFD.⁷ Kinetics evidence and the other experimental data^{3,7} also testify in favour of absence of any other routes (including those involving participation of radicals) of the reaction except that depicted in Scheme 1 (path (a)). In particular, very low frequency factor values ($\log A \sim 6.6$ – 10) noted^{7a,c} for oxidation of alkanes by TFD are regarded as support for the existence of a highly ordered transition state preceding the formation of reaction products.

‡ PS spectrum of TFP was recorded on Hitachi MPF-4 fluorimeter at 77K ($\lambda_{\text{exc}} = 320$ nm): the spectrum has a broad maximum in the region 400–490 nm (spectrum of PS of TFP recorded in gas phase⁸ has a shift to longer wavelength region at *ca.* 30 nm).

§ Estimation of the yield of excitation of TFP^*_T was made on the assumption that the quantum yield of its PS is about equal to that of acetone, *i.e.* 10^{-5} . Under this approach, the yield of chemiexcitation of TFP was estimated to be 10^{-4} and 10^{-5} for the reaction of TFD with AD and DMB respectively.

¶ We have observed CL occurring upon interaction of TFD and DMD with various types of organic compounds including some polyaromatic hydrocarbons, dyes (rhodamine 6G, eosine), europium chelates *etc.* CL intensities recorded in these reactions in many cases are significantly higher than those observed in the reaction of dioxiranes with Ad and DMB (unpublished results). The study of CL arising in reactions of organic compounds with dioxiranes is under progress in our laboratory.

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