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# Maximization of the Chemiluminescence Efficiency of 1,4,5-Triarylhydroperoxy-4H-isoimidazoles

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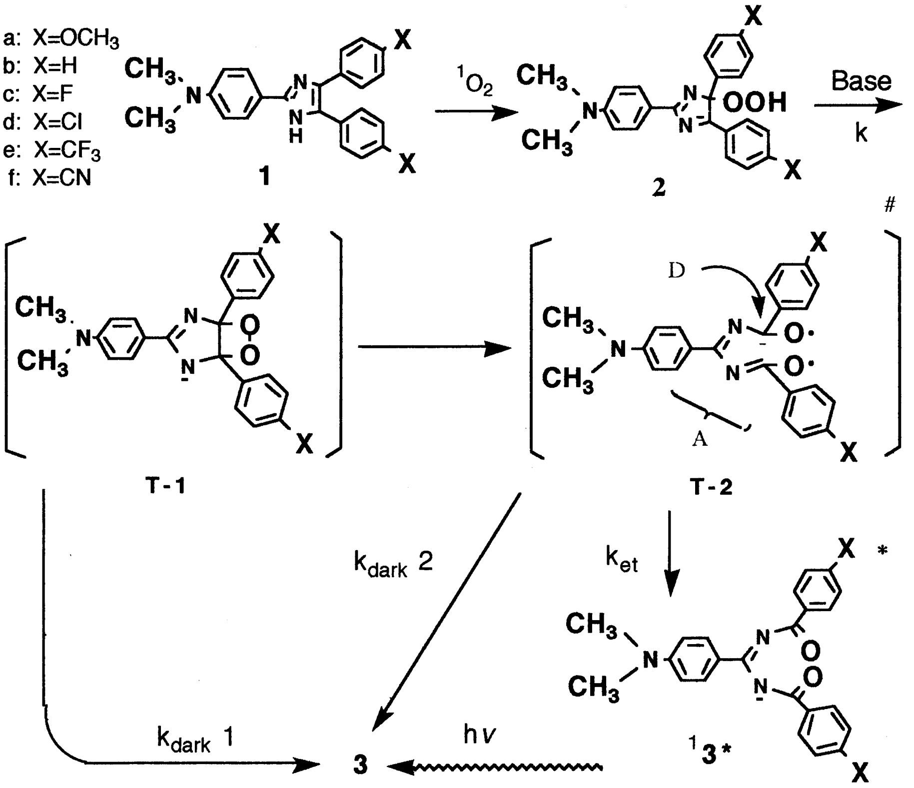
A bell shape correlation curve has been found for a plot of the Hammett $\sigma$ constant and the quantum yields of the formation of excited amidines from the chemiluminescent reaction of 2-(p-dimethylaminophenyl)-4,5-di( p-X--phenyl)-4-hydroperoxy-4H-isoimidazoles (X= $OCH_3$, H, F, Cl, $CF_3$, and CN) with bases.

One of the major goals in the study of chemiluminescence is the maximization of the yields of excited states.1) In their studies on the chemiluminescent reaction of triarylimidazoles with oxygen and base, Philbrook and Maxwell found a linear Hammett relationship between the chemiluminescence efficiencies and the $\sigma$ values of the substituents at the para position of the 2-phenyl group.2) They observed that the efficiency increases as the electron donating ability increases. These reactions proceed *via* hydroperoxyisoimidazoles; corresponding diarylamidines are the sole final products and they are the light emitters in the reactions (Scheme 1).3) During our efforts to construct of an efficient chemiluminescent system, we found that 2-(p-dimethylamino-phenyl)-4,5-di-(p-fluorophenyl)-4-hydroperoxy-4H-isoimidazole (**2c**) is the most efficient member of the series examined so far; the efficiency of formation of the excited singlet amidine ($^1$**3c***) is 79%. Electron transfer steps have been proposed for most chemiluminescent reactions producing singlet states.4) Under the assumption that electron transfer is also involved in the chemiluminescence of the imidazoles, we have examined a series of 2-(p-dimethylaminophenyl)- 4,5-di(p-X-phenyl)-4-hydroperoxy-4H-isoimidazoles [X: (a) $OCH_3$, (b) Cl, (c) ,F, (d) H, (e) $CF_3$, (f) CN] (**2a-f**). In this system electron releasing groups at the 2-position and electron attracting groups at the 4- and 5-positions lead to maximum light emission. Compounds **1a-f** were prepared by the method of White et al.3) Oxidation of compounds **1a-f** with $^1O_2$ (generated by methylene blue photosensitization at -78 °C) gave the corresponding hydroperoxides **2a-f** in fairly good yields.5) The corresponding amidines **3a-f** were isolated from the reaction of **2a-f** with KOH in methanol.6) Chemiluminescent emissions were measured by means of a photodiode array (PMA, HAMAMATU PHOTONICS) which recorded integrated light yields in terms of the number of photons. The chemiluminescent light emission was counted by PMA upon addition of 0.2 ml of 1M KOH in methanol to 1ml solution of the hydroperoxides ($10^{-3}$-$10^{-4}$M) in $CH_2Cl_2$.3,7) The chemiluminescent efficiency ($\Phi$cl) was determined by comparing the total amount of light emitted with light emission from the standard luminol chemiluminescence.8) The results are summarized in Table 1. In general, an over all quantum yield of a chemiluminescent reaction is defined as,

$$\Phi cl = \Phi r \cdot \Phi ex \cdot \Phi f \qquad (1)$$

where $\Phi_r$ is the product yield of the emitter, $\Phi_{ex}$ is the efficiency of the formation of singlet excited state, and $\Phi_f$ is the fluorescence quantum yield of the emitter. In order to estimate $\Phi ex$ , $\Phi f$ and $\Phi r$ (≈1) were measured under the conditions employed in the reaction (Table 1). $\Phi ex$ was estimated using Eq.1. The Hammett plot of $\Phi ex$ is shown in Fig.1. This plot is clearly nonlinear (bell shaped) is



Scheme 1.

Table 1.6) Relative Chemiluminescence Yields ($\Phi cl_X/\Phi cl_o{}^{a)}$) and Chemiluminescence Quantum Yields ($\Phi cl_X$) of Lophineperoxides **2**, Fluorescence Quantum Yieds ($\Phi f_X$) of Amidines **3** and Quantum Yields {kex/(kdark2+kex)=$\Phi ex_X$} of Formation of Amidies in Excited Singlet State $^1$**3***

| | Substituents=X(σ) | | $\Phi cl_X/\Phi cl_o$ | $\Phi cl_X$ | $\Phi ex_X$ | | $\Phi f_X$ |
|---|---|---|---|---|---|---|---|
| **2a:** | CH3 0 | (0.27) | 97 | 7.0x10$^{-3}$ | 3.0X10$^{-1}$ | **3a :** | 2.3X10$^{-2}$ |
| **b :** | H | (0.00) | 51 | 3.7X10$^{-3}$ | 5.3X10$^{-1}$ | **b :** | 7.0X10$^{-2}$ |
| **c :** | F | (0.062) | 140 | 1.0X10$^{-2}$ | 7.9X10$^{-1}$ | **c :** | 1.3X10$^{-2}$ |
| **d :** | Cl | (0.23) | 64 | 4.6X10$^{-3}$ | 4.0X10$^{-1}$ | **d :** | 1.2X10$^{-2}$ |
| **e :** | CF3 | (0.54) | 6.6 | 4.8X10$^{-4}$ | 1.1X10$^{-1}$ | **e :** | 4.2X10$^{-3}$ |
| **f :** | CN | (0.66) | 0.77 | 5.5X10$^{-5}$ | 2.7X10$^{-3}$ | **f :** | 2.0X10$^{-2}$ |

a) $\Phi cl_o$ is the chemiluminescent quantum yield of lophine peroxide (**2g**) as the standard substance.

maximized at the σ value of fluorine ($\sigma_F$). Surprisingly, the value of Φex (0.79) is comparable to that measured for firefly bioluminescence.⁹⁾ The chemiluminescent reaction of **2** may involve cyclization (k) *via* an intramolecular Michael type addition affording the corresponding dioxetane **T-1**, followed by a retro[2+2]cycloaddition of **T-1** providing an anion intermediate **T-2** (Scheme 1) through an adiabatic process. Subsequenly, an intramolecular electron reorganization or electron transfer from an electron donor moiety (D) to an electron accepting moiety (A) may take place through a diabatic process ($k_{ex}$) to give $^1$**3***. That is, we propose that the generation of a pair of diradicals **T-2** holding an unstable anion enables the system to afford the excited products through an exothermic electron transfer step similar to mechanisms advanced by Wilson, McCapra and Shuster.4) The exothermic electron transfer rates may have an inverted region as suggested by the Marcus theory; this bell shape relationship may be attributable to the presence of an exothermic electron transfer step consistent with the high Φex.10,12) The chemiluminescent decay rates (k) follow pseudo first-order kinetics. A plot of log $k_X/k_H$ measured at 15 °C against σ values gave a straight line with ρ value 1.59 (r= 0.976) measured by least squares method.11) The rate determine step appeared to be the nucleophilic ring closure to give the dioxetane intermediate **T-1**. It is notable that the rate determining step and the chemiluminescent efficiency determining step are clearly independent.These observationsare consistent with an electron transfer mechanism. We would like to point out the advantages of the imidazole system for generating excited products in the singlet state.

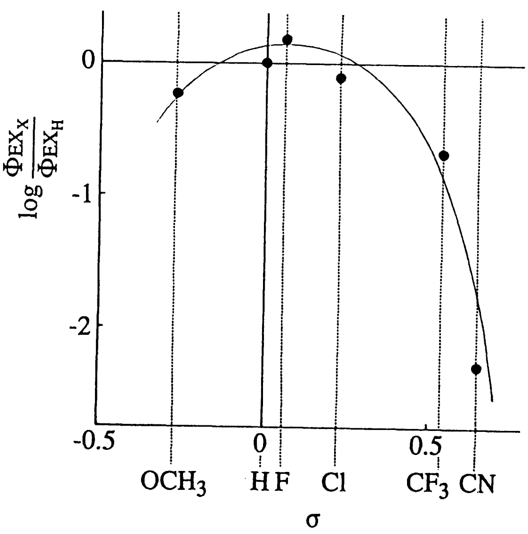


Fig. 1.Hammett plot of log ($\Phi ex_X/\Phi ex_H$).

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5) $^1$HNMR, IR, CHN analysis data for new hydroperoxides **2c, 2d, 2e, 2f**, and **2g** are as follows. **2c**: Mp 105-108 °C,$^1$HNMR(500 MHz, $CDCl_3$) δ 3.06 (s, 6H), 6.52 (bs, 2H), 7.00 (t, J=8.8 Hz, 2H), 7.43 (dd, J= 8.8 Hz, J= 4.8 Hz, 2H), 8.06(bs, 2H), and 8.35 (dd, J=8.8 Hz, J=4.8 Hz,2H); IR $\upsilon_{max}$ 1603 (C=N) cm$^{-1}$,1234 (C-F), and 766 ( phenyl); Anal. Found: C,67.21; H,4.55; N,10.08%. Calcd for $C_{23}H_{19}N_3O_2F_2$: C,67.812;H,4.70;N,10.31%; **2d:** Mp 117-122 °C;$^1$HNMR(500 MHz, $CDCl_3$, -10 °C) δ 3.15 (s, 6H), 6.90 (d, J=9.0 Hz, 2H), 7.31(d,J= 8.5 Hz, 2H), 7.40 (d,J= 8.5 Hz, 2H), 7.56 (d, J= 9.0 Hz, 2H), 8.23 (d, J= 8.5 Hz, 2H), and 8.32 (dd,J= 8.5 Hz, 2H); IR $\upsilon_{max}$ 1603(C=N) cm$^{-1}$, 1095(C-Cl), and 824 (phenyl); Anal. Found: C,62.30; H,4.23;N,9.40%. Calcd. for $C_{23}H_{19}N_3O_2Cl_2$: C,62.74;H,4.35,N,9.40%. **2e,** Mp 126-128°C; $^1$HNMR (500 MHz, $CD_3CN$) δ 3.05 (s, 6H), 6, 73 (d, J= 9.0 Hz, 2H), 7.51 (d, J= 8.5, 2H), 7.64 (d, J= 8.5 Hz, 2H), 7.81(d, J= 8.2 Hz, 2H), 8.12 (d, J= .9.0 Hz, 2H), and 8.34 (d, J= 8.2 Hz, 2H); IR $\upsilon_{max}$ 1605 (C=N) cm$^{-1}$, 1095 (C-F ) ; Anal. Found: C, 58.77; H, 3.64; N, 8.00%.Calcd. for $C_{25}H_{19}N_3O_2F_6$: C,59.18; H,3.77; N,8.28%. **2f**: Mp 162-164 °C $^1$HNMR (500 MHz, $CDCl_3$) δ 3.07 (s, 6H), 6.55(m, 2H), 7.47 (d, J= 6.6 Hz, 2H),7.62(d, J=6.5 Hz, 2H),7.68(d, J=6.4 Hz, 2H), 8.02(m, 2H), and 8.34 (d, J=6.4 Hz, 2H); IR $\upsilon_{max}$ 2230 (CN) cm$^{-1}$, 1601 (phenyl); Anal. Found: C,70.95; H,4.49; N,16.21%.Calcd. for $C_{25}H_{19}N_5O_2$:C,71.25; H,4.51; N,16.62%. **2g:** Mp 108- 110 °C (Lit,110 °C)3) $^1$HNMR (500 MHz, $CDCl_3$) δ 7.22 (t, J= 7.2 Hz, 2H), 7.30-7.36 (m, 4H), 7.46-7.55 (m, 4H), 7.59 (t, J= 7.2 Hz, 1H); IR (KBr) $\upsilon_{max}$ 1613 (C=N) cm$^{-1}$, and 766 (phenyl).

6) The corresponding amidines are the light emitters because $\lambda_{max}$ of their fluorescence spectra much those of the chemiluminescence spectra noted earlier by White and Harding. E. H. White, D. F.Rosewell, A.C.Dupon, and A. A.Wilson,*J.Am.Chem.Soc.*, **109**, 5189 (1987).

7) $CH_2Cl_2$ was chosen from three solvents($CH_2Cl_2$, methanol and DMSO) as the most suitable solvent for maximizing light emission.

8) The quantum yield of lophine peroxide**2g** ($\Phi cl_0$=7.2X10$^{-5}$) was calculated using luminol as chemiluminescence standard(Φ=0.0083), J. Lee, A. S. Wesly, J. F. III. Ferguson, and H. H.Seliger,"Bioluminescence in Progress," ed by F. H. Johnson and Y. Haneda, Princeton University Press, Princeton (1966) p. 35; $\Phi cl_X$ was calculated based on the chemiluminescence efficiency of **2g** as the standard (duplicate runs). $\Phi f_X$ was calculated based on the fluorescence efficiency of 9,10- diphenylanthracene (0.81) as a standard. I. B. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules," Academic Press New York and London (1965), p.14.

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11) The σ constants are taken from McDaniel, D. H; Brown, *J, Org. Chem..*,**23**, 420 (1958). The sign of ρ (+) suggests that the rate determined step is the reaction of the hydroxy group with the isoimidazole π system.

12) A correlation between a $\sigma x$ value and a driving force($\Delta G$) is $const\cdot(\sigma-\sigma_F)= (\lambda+\Delta G)/(4\lambda k_BT)^{1/2}$, where λ= a Marcus parameter, $k_B$= the Boltzmann constant, and T= the absolute temperaturue.

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