# An Unusual Occurrence of Chemiluminescence resulting from Metal–Ammonia Reductive Dehalogenation Reactions

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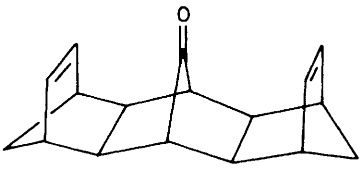
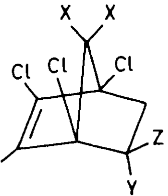
Birch type reductive dehalogenation of some members of the series of norbornenes (**2a**—**h**), (**4i**) proceeds with chemiluminescence; an explanation for this phenomenon is advanced.

In connection with our projected synthesis of the trimethanoanthracenone (**1**) and related compounds quantities of 2-substituted-7,7-dimethoxynorbornenes (**3**) were required. These compounds were obtained through Birch type reductive dehalogenation of the tetrachloro precursors (**2**) (*i.e.* alkali metal, ethanol proton source, liquid $NH_3$, tetrahydrofuran, THF) according to the procedure of Jung and Hudspeth.[1] During the course of this work we were surprised to observe strong chemiluminescence accompanying the reduction of (**2a**) and (**2b**). The unusual conditions giving rise to this chemiluminescence[2] and its relevance to the still unresolved, yet much debated, mechanism of dissociation of aromatic and vinylic halide anion radicals[3–5] prompted us to study it further. Herein are reported our preliminary findings which define more precisely the requirements for its occurrence.

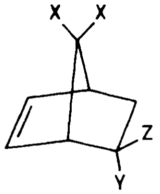
Dropwise addition of a solution of (**2a**) in ethanol and THF to a solution of sodium in liquid ammonia† at −33 °C resulted in an *immediate* emission of a bright green light which persisted, but with diminishing intensity, as the addition progressed and finally ceased when the sodium had been totally consumed. Crude spectroscopic analysis‡ revealed the light to be a broad continuum spanning the green region of the spectrum.



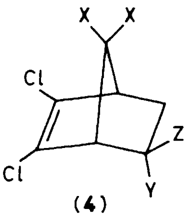
(**1**)



(**2**)



(**3**)



(**4**)

**a**; X = OMe, Y = OH, Z = H
**b**; X = OMe, Y = OAc, Z = H
**c**; X = OMe, Y = $OBu^n$, Z = H
**d**; X = OMe, Y = H, Z = H
**e**; X = Cl, Y = OH, Z = H
**f**; X = H, Y = OH, Z = H
**g**; X = H, Y = H, Z = OH
**h**; X = OMe, Y = $CO_2Et$, Z = H
**i**; X = H, Y = $OBu^n$, Z = H

Experiments carried out on the reduction of (**2a**) revealed that the chemiluminescence, in terms of colour and intensity, is *independent* of the following variables: (i) *the nature of the reducing metal* (Li, Na, or K are equally efficacious); (ii) *ion-pairing effects* (chemiluminescence was still observed when the reduction was carried out using equimolar amounts of Na and cryptand [222]§); (iii) *the proton source* (in fact the chemiluminescence was unabated even in the absence of alcohol); (iv) *temperature* (the chemiluminescence was just as pronounced at −83 as at −33 °C).

Birch reductions of (**2b**—**h**), (**3a**), and (**4i**) were carried out† and the results are given in Table 1. Perusal of these data reveals the following substituent requirements for producing chemiluminescence: (i) the vinylic halogens, but not those attached to C-1 and C-4, are essential (*cf.* entries 1, 9, and 10); (ii) the presence of either an *endo*- or *exo*-2-oxy substituent appears to be mandatory (*cf.* entries 3, 4, 6, 7, and 8); (iii) the intensity of chemiluminescence depends on the identity of the 2-oxy substituent Y, being strongest for Y = OH and weakest for Y = $OBu^n$ (*cf.* entries 1–3); (iv) 7-substituents having lone pairs of electrons enhance chemiluminescence (*cf.* entries 1, 5, and 6) but those at positions 1 and 4 do not (*cf.* entries 6 and 10).

We propose that the chemiluminescence is due to the dissociation of the vinylic C–Cl bond of the anion radical of the substrate, say (**2a**), giving rise to a substantial number of vinyl radicals in the excited $^2\Pi$ state which then fluoresce to their $^2\Sigma$ ground state. This transition is estimated to be 2.4 eV[4] which is consistent with the energy of the emitted green light *viz.*, 2.2.—2.5 eV. If this proposal is correct then our data

**Table 1.** Birch reduction data (Na,[a] EtOH proton source) of (**2**), (**3a**), and (**4**).

| Entry | Substrate | Product[b] | Chemiluminescence?[c] |
|---|---|---|---|
| 1 | (**2a**) | (**3a**) | Strong |
| 2 | (**2b**) | (**3a**)[d] | Medium–strong |
| 3 | (**2c**) | (**3c**) | Medium |
| 4 | (**2d**) | (**3d**) | None |
| 5 | (**2e**) | (**3f**)[d] | Medium–strong |
| 6 | (**2f**) | (**3f**) | Medium |
| 7 | (**2g**) | (**3g**) | Medium |
| 8 | (**2h**) | (**3h**)[d,f] | None |
| 9 | (**3a**) | (**5**)[e] | None |
| 10 | (**4i**) | (**3i**) | Medium |

[a] The results were found to be the same using Li or K in place of Na. [b] Yields were generally 80% (by g.l.c.). [c] The classification of the light intensity is based on visual observations of experiments carried out in a completely dark room. It is obviously crude but serves a useful purpose. [d] Yield 30% + intractable mixture. [e] *endo*-7,7-Dimethoxynorbornan-2-ol. [f] Y = $CH_2OH$.

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† Identical conditions were employed throughout this work: substrate (2 mmol) in THF (10 ml); alkali metal (16 mmol) in liquid ammonia (75 ml).

‡ An Erma C-825A hand spectroscope was used.

§ This reagent is known to encapsulate completely $Na^+$ ions in liquid ammonia thereby destroying any ion pairs involving the latter species: P. Gans, J. B. Gill, and J. N. Towning, *J. Chem. Soc., Dalton Trans.*, 1977, 2202.

constitute the first examples of the chemiluminescent mode of dissociation of anion radicals of vinylic halides. These species normally dissociate non-radiatively through an adiabatic pathway which leads directly to the ground state $^2\Sigma$ vinyl radical from the $^2\Pi$ vinyl halide anion radical. The adiabatic switching between the $^2\Sigma$ and $^2\Pi$ states is brought about by concomitant carbon–halogen fission and pyramidalization of the olefinic carbon atom.[5,6] It seems, then, that a combination of geometric and electronic (substituent) effects in (**2**) make the non-adiabatic dissociation of the anion radicals of these species to the excited $^2\Pi$ vinylic radicals competitive with the adiabatic pathway. We are currently investigating why this is so.

*Added in proof:* We have subsequently found that the bromo analogues of (**2**) chemiluminesce upon Birch reduction, as do *p*-chlorophenol and 6-bromo-2-naphthol.

We thank the Australian Research Grants Scheme for support and Professor K. D. Jordan for helpful discussion.

*Received, 31st August 1983; Com. 1166*

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