ELECTRON EXCHANGE CHEMILUMINESCENCE FROM A STERICALLY STABILIZED CYCLOBUTADIENE-1,2-DIOXETANE

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SUMMARY: The rather stable 1,2-dioxetanes (2) and (3), derived from the steri-
cally stabilized cyclobutadiene (1), exhibit distinct enhanced chemiluminescence
behavior, namely energy transfer chemiluminescence (ETC) for (2) and electron
exchange chemiluminescence (EEC) for (3).

The dioxetane (2) and its epoxide (3), both derived[1] from the sterically
stabilized cyclobutadiene (1), count among the most strained[2] stable dioxetanes
that are known to date (Eq.1). At elevated temperatures (ca. 100-120°C) the
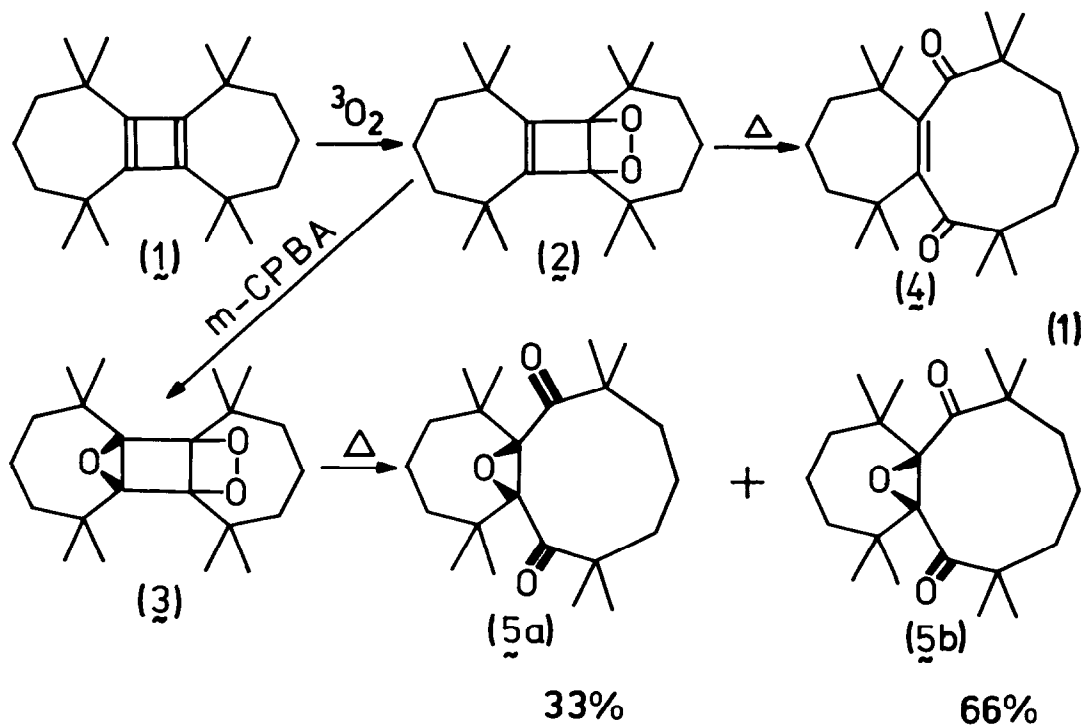
respective diones (4) and (5a,b)[3] are produced, accompanied by direct chemi-
luminescence.[1] Besides the surprising thermal stability of these strained
"high energy" molecules, we were intrigued by the observation that the in-
tensity of direct chemiluminescence was significantly larger for the epoxide
derivative (3) compared to (2). Consequently, we decided to investigate in
detail the activation and excitation parameters of these unusual dioxetanes.
The results of our investigation are that (3) gives enhanced chemiluminescence
with oxidizable polycyclic aromatic fluorescers such as rubrene via the electron
exchange mechanism[4], while (2) shows enhanced chemiluminescence via the energy
transfer mechanism. To the best of our knowledge represents (3) one of the first
dioxetanes[5] that exhibits _intermolecular_ EEC, a behavior which so far had been
limited to the α-peroxylactones[6]. The dioxenedioxetanes[7,8] contain oxidizable
substituents and operate, therefore, via _intramolecular_ EEC.

The activation parameters of dioxetanes (2) and (3) were determined by chemi-
luminescence techniques. In both cases clean first order kinetics were obtained
for the direct and fluorescer-enhanced chemiluminescence. Neither dioxetane
showed fluorescer concentration dependence on the rates. The values are for
$\Delta G^{\neq}$ (373°K) 28±3 and 29±2 (29.7) kcal/mol, for $\Delta H^{\neq}$ 30±2 and 27±1 (29.2) kcal/mol
and for $\Delta S^{\neq}$ +7±4 and -5±2 (-1.4) cal/mol $^{\circ}$K, respectively for (2) in toluene
between 350-370°K and (3) in xylene between 370-400°K.[9]

Surprising was the much more intense direct chemiluminescence, i.e. the
ϕ^{DC} values are 0.0094 x 10^{-4} and 9.0 x 10^{-4} einstein/mol (ca. 10% error),
respectively exhibited by (2) and (3). Although the fluorescence spectra of
the diones (4) and (5a,b), matched qualitatively the direct chemiluminescence
spectra of (2) and (3)[10], respectively, too little authentic material of the
diones was available to enable determination of their absolute fluorescence
yields. However, the relative fluorescence yields of the diones could be esti-
mated by photophysical excitation of spent equimolar solutions of the indi-
vidual dioxetanes, affording ϕ^{fl}(5a,b)/ϕ^{fl}(4)∿40.Consequently, the more efficient
direct chemiluminescence of dioxetane (3) is only in part a consequence of

the much greater fluorescence efficiency of dione $(\underset{\sim}{5a,b})$. Since $\phi^{DC}=\phi^{S}\cdot\phi^{fl}$, the ratio of singlet yields of the excited diones $(\underset{\sim}{5a,b})$ and $(\underset{\sim}{4})$ from dioxetanes $(\underset{\sim}{3})$ and $(\underset{\sim}{2})$, respectively is $\phi^{S}(\underset{\sim}{3})/\phi^{S}(\underset{\sim}{2}) \sim 22\pm3$. Thus, dioxetane $(\underset{\sim}{3})$ is a more efficient thermal source of excitation.[11] To determine the singlet (ϕ^{S}) and triplet (ϕ^{T}) yields of dioxetane $(\underset{\sim}{2})$, we employed enhanced chemiluminescence techniques, using 9,10-diphenylanthracene (DPA) for ϕ^{S} and 9,10-dibromoanthracene (DBA) for ϕ^{T}.[12] The DPA and DBA fluorescers gave good linear double reciprocal plots of the emission intensity versus fluorescer concentration, confirming energy transfer excitation of the fluorescer by the chemienergized dione $(\underset{\sim}{4})$. The ϕ^{S} and ϕ^{T} values are 0.003% and 0.19% (ca. 10% error), respectively. Clearly, $(\underset{\sim}{2})$ is a typical dioxetane, showing a large preference for triplet excitation $(\phi^{T}/\phi^{S}$ ca. $65\pm10)$, but the total efficiency of chemiexcitation is very low $(\phi^{T+S}$ ca 0.2%).

The DPA-enhanced chemiluminescence intensity of $(\underset{\sim}{3})$ was a linear function of the DPA concentration, instead of the expected double reciprocal dependence for energy transfer excitation. We suspected EEC as excitation route and confirmed it by demonstrating a linear semilogarithmic dependence between the fluorescer emission intensities (ln I_{o}) and their oxidation potentials (E_{ox}), using rubrene, naphthacene, perylene and DPA as fluorescers.[13] However, it is important to mention that, like for other examples[14], in this case of EEC the fluorescers do not affect the rate of dioxetane decomposition.

Dioxetane $(\underset{\sim}{3})$ constitutes one of the few examples[5] for which chemienergization by intermolecular electron exchange operates. Apparently the inductive effect of the epoxide functionality lowers sufficiently the reduction potential of dioxetane $(\underset{\sim}{3})$ compared to $(\underset{\sim}{2})$ to make electron transfer between dioxetane $(\underset{\sim}{3})$ and fluorescer (Fl) energetically accessible. Also, the additional strain energy due to the epoxide ring could be a factor in promoting the intermolecular EEC of this system. It seems, therefore, advisable to search for other electron deficient and highly strained dioxetanes for the purpose of electron exchange studies.

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3. Diones (5a,b) are locked-in conformational isomers with respect to the carbonyl groups. In the thermolysis of dioxetane (3) both conformers (5a,b) are formed, but on photolysis of (3) only (5a) is produced. On heating (5a) affords the same mixture of (5a,b) as in the thermolysis of (3).

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9. The values in parentheses for dioxetane (3) have been determined by quantitative ^{1}H-NMR in d_8-toluene at 363-383°K. A detailed discussion of the differences in the thermal stability of dioxetanes (2) and (3) is reserved for a full paper.

10. For dione (5) the observed fluorescence corresponds to both conformers (5a,b), while the direct chemiluminescence of dioxetane (3) is presumably due to conformer (5a).

11. It is assumed here that the isomeric diones (5a) and (5b) display comparable fluorescence yields; however, the pure isomers (5a) and (5b) were not available in sufficient amounts to determine their relative fluorescence yields.

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13. The respective ln I_0 (ca. 15% error) values are 7.42±0.81, 7.23±0.95, 6.48±1.06 and 5.70±1.22 and the respective E_{ox} values are 0.82, 0.95, 1.06 and 1.22 V.

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