

# CHEMILUMINESCENCE IN SOLUTION

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Most existing evidence points to the fact that visible chemiluminescent emission from reactions in solution arises from the production of molecules in their lowest singlet excited states, such molecules being of types capable of fluorescence. Chemiluminescence is, in fact, fluorescence excited by chemical action. The emitting molecules must have absorption bands in the visible or near ultraviolet region, and the reaction by which they are formed must liberate energy of at least 40–80 kcal/mol. Triplet excited states have lower energies than the corresponding singlet states, but because of their long radiational life they are usually very efficiently quenched by collisions in liquid media before radiating.

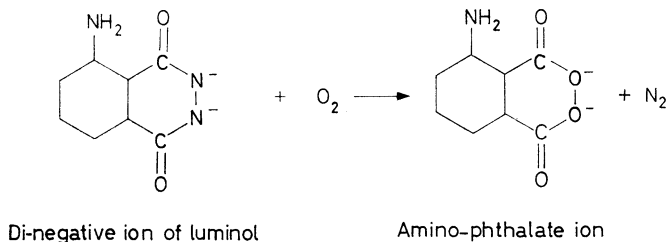
For enough energy to be located on individual molecules to permit visible radiation to be emitted the reaction must be a very energetic one. Oxidation reactions with molecular oxygen or hydrogen peroxide, or the breakdown of organic hydroperoxides, form practically all types of chemiluminescent reactions. Radical intermediates are involved, and the course of the reaction is usually a matter of speculation only. The identification of the emitter is also a less simple problem than might appear, because fluorescent bands are not always sharply diagnostic. These are the two central problems of chemiluminescence. The chemical structures of molecules primarily involved in luminescence are usually known; even those in living organisms are yielding to intensive attack by organic chemists. Their reaction mechanisms on oxidation, however, are still in most instances obscure.

The bimolecular recombination of radicals such as  $C_6H_5 + C_6H_5 \rightarrow$  diphenyl does not seem usually to lead to emission. The evolved energy is largely concentrated in the newly-formed bond and is quickly removed by thermal equilibration. A reaction, due to Kurtz, which may have a simple mechanism is as follows<sup>1</sup>.

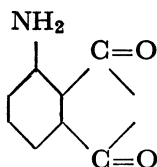
Dibenzanthrone (R) in chloroform, treated with chlorine, forms the cation  $R^+$ . When aqueous hydrogen peroxide and alkali are added, and more chlorine passed in, a bright red chemiluminescence is emitted, apparently the same as the fluorescence of dibenzanthrone, while scarcely any permanent oxidation of the dye occurs. This could be explained by the reaction,  $R^+ + O_2^- \rightarrow R^* + O_2$ , followed by  $R^* \rightarrow R + h\nu$ . There is no certainty, however, that the actual mechanism takes this course instead of a more complex one.

The oxidation of luminol, 3-amino phthalic cyclic hydrazide, because of the brilliance of its chemiluminescence, has given rise to a great number of investigations, which, however, have mostly served merely to show the complexity of the mechanism. The reaction is usually carried out in

aqueous alkaline hydrogen peroxide solution to which hypochlorite solution is added<sup>2</sup>. The quantum light yield is then about  $10^{-3}$ , but yields of 5 per cent are found if the substance is dissolved in dimethyl sulphoxide solution with added solid potassium hydroxide and oxidized by air<sup>3</sup>. E. H. White has shown that the reaction is more free from complications in the latter solvent; each luminol molecule requiring two molecules of base and one of  $O_2$ , and forming the amino-phthalate ion, which is identified as the emitter:



The identity of the chemiluminescent emission with the fluorescence of amino-phthalate ion shows that the latter is formed (to the extent of at least 50 per cent) in its singlet excited state. The chemical energy of the reaction is enough for this to be possible, but there remains the question as to how it becomes so located on the product molecule. White suggests that an oxygen adduct in a triplet state is involved, and that an intersystem crossing triplet-singlet occurs after nitrogen elimination. Another possibility is that successive attack by two  $O_2$  molecules removes two electrons through semiquinone stages,  $N_2$  is eliminated, and the diradical



formed, which may add on  $O_2^{2-}$  to give the final product.

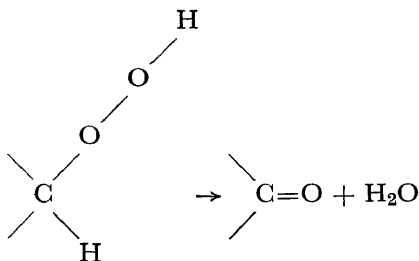
Another notable chemiluminescent oxidation, that of *NN'*-dimethyl biacridylum nitrate (lucigenin), is not yet fully understood. In dilute, hot solution the emission (blue) is from the energy-rich product molecule methyl acridone, but in cold strong solution the emission is green<sup>4</sup>. This fact is suggestive of an energy-transfer mechanism raising some of the reactant molecules to the fluorescent state.

The mechanism of the oxidation of siloxene derivatives and the nature of the emitters are still obscure. As shown by Kautsky, quanta corresponding to 60 kcal/mol are emitted, and striking energy transfer effects to red-fluorescent dyes adsorbed on the materials are observed<sup>5</sup>.

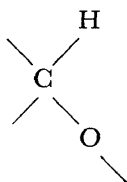
9:10-dihydroxy anthracene autoxidizes in aerated benzene solution, with light emission, to give a quinone and hydrogen peroxide, presumably *via* the semi-quinone stage. Whether the emitter is the parent substance or not is unknown. Under alkaline conditions the mechanism of oxidation changes and no light is emitted<sup>6</sup>.

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The thermal decomposition of organic hydroperoxides in presence of fluorescent substances often leads to chemiluminescence. The significant product appears to be a ketone, and about 70 kcal/mol are liberated:



The added fluorescent substance which receives the energy of reaction remains largely unchanged. An example is tetralin hydroperoxide with zinc tetraphenylporphin, studied by Linschitz<sup>7</sup>. A plausible interpretation is the removal of an electron from the porphin molecule, turning the peroxide to OH<sup>-</sup> and the radical

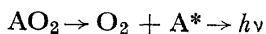


followed by one of several possible reactions which restore the electron, reforming the porphin molecule, raised to its excited state, and yielding the final products of a ketone and water. Alternatively, H-atom abstraction may be substituted for electron removal. Energy transfer is another mechanism. In the thermal oxidation of hydrocarbons such as ethyl benzene, with traces of anthracene derivatives present, chemiluminescence corresponding to the anthracene fluorescence has been observed by Vassil'ev<sup>8</sup>. Two key facts are that the chief oxidation product is a ketone and that the intensity of luminescence is increased when heavy atoms, such as bromine, are substituted into the anthracene. A good case can therefore be made out that the ketone is formed in its triplet state, and transfers its electronic energy to the anthracene on near collision; this formally forbidden triplet-singlet energy transfer being allowed by spin-orbit interactions.

There exists still a third possibility, that of *P*-type delayed fluorescence<sup>9</sup>. Thermally produced ketone products in triplet states might transfer their energy on collision to anthracene molecules to endow them with triplet energy, followed by bimolecular interaction of anthracene triplets to give an excited and a ground pair of singlet states. Because of the readiness by which triplet states of aromatic hydrocarbon molecules are quenched by dissolved oxygen this process could not lead to high yields of output.

Dufraisse and his school have shown that a number of cyclic peroxides of aromatic hydrocarbons chemiluminesce when heated<sup>10-12</sup>. The peroxides

decompose to give oxygen and the hydrocarbon, and the emission seems to correspond to the fluorescence of the latter. However, this simple scheme:



is not possible, as the heat of reaction is far too small to give quanta in the blue region of the spectrum<sup>13</sup>. The dissociation process in some instances occurs to an extent of 95 per cent, and the question arises as to whether the light emission comes from the small irreversible part of the decomposition, or whether some build-up of energy by intermediates occurs. That the latter is probable seems to agree with the fact that the stronger luminescence effects are associated with these peroxides which dissociate reversibly the most efficiently.

The photochemical formation of these cyclic peroxides has curious kinetics, and triplet levels, excited hydrocarbon dimers, diradical oxides, and excited oxygen molecules have all been postulated<sup>14-16</sup>.

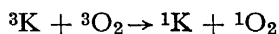
Footo has now demonstrated (unpublished work) that excited oxygen molecules are the active intermediates. The reverse dissociation  $\text{AO}_2 \rightarrow {}^1\text{O}_2^* + {}^1\text{A}$  cannot directly explain the chemiluminescence. The alternative  $\text{AO}_2 \rightarrow {}^3\text{O}_2 + {}^3\text{A}$ , followed by  ${}^3\text{A} + {}^3\text{A} \rightarrow {}^1\text{A} + {}^1\text{A}^*$  seems most likely.

An intriguing and puzzling form of chemiluminescence which is an emission by the oxygen molecule has been under recent investigation. Earlier workers had noted a red glow in reactions between hydrogen peroxide and hypochlorite or chlorine, and Khan and Kasha<sup>17</sup> found two narrow spectral bands at 15788  $\text{cm}^{-1}$  and 14221  $\text{cm}^{-1}$ . Since these are separated by almost exactly the vibrational frequency of the ground level of the  $\text{O}_2$  molecule they identified them as the 0,0 and 0,1 bands of the forbidden  ${}^1\Sigma_g^+ \rightarrow {}^3\Sigma_g^-$  transition. The corresponding gas-phase bands are 2593  $\text{cm}^{-1}$  lower in frequency, which would have to be explained as an unusually large solvent shift.

More recent measurements by Browne and Ogryzlo<sup>18</sup> have shown the presence of eight bands, all due to emission from gaseous oxygen dropping from an excited to the ground state. These fall into three groups, the 0-0 and 1-0 transitions from the  ${}^1\Delta_g$  state at 7800 and 9300  $\text{cm}^{-1}$ , the 0-0 0-1, and 1-1 transitions from the  ${}^1\Sigma_g^+$  state at 13100-11600  $\text{cm}^{-1}$  and the 0-0, 0-1, and 1-0 transitions from a weakly bound complex of two  ${}^1\Delta_g$  states at 17200-14300  $\text{cm}^{-1}$ . These remarkable observations raise many questions difficult to answer. The overall reaction giving chloride ion, water, and oxygen, is very energetic, but precisely how the oxygen molecule is excited and whether one molecule or some intermediate such as  $\text{HOCl}$  reacts, or whether two need to co-operate, is unknown. McGrath and Norrish<sup>19</sup> have shown that, in certain reactions involving oxygen atoms, vibrationally excited oxygen molecules with up to 70 kcal/mol are formed, but atoms do not participate here. The production of dimer  ${}^1\Delta_g$  complexes either indicates a stage liberating two excited  $\text{O}_2$  molecules simultaneously, or more likely, is due to the long life-time of the state. The dimer complex has a permitted radiational transition to the ground state of two normal  $\text{O}_2$  molecules, but radiation from the  ${}^1\Sigma_g^+$  state, and particularly from the  ${}^1\Delta_g$  state itself, is strongly forbidden. To allow of all the emission observed

the newly formed excited molecules must find themselves in a perturbing environment before they ultimately break free as gas. Whatever explanations may ultimately emerge, it is clear that the  $O_2$  molecule, with its unusual triplet ground state, shows many unexpected strange features in its behaviour. The chemistry of the excited oxygen molecule is now being studied. Foote, as indicated above, has succeeded in preparing cyclic peroxides by oxidation with a hydrogen peroxide hypochlorite mixture. Waters has interpreted the formation of singlet  $O_2$  as arising from those heterolytic reactions which involve electron-pair movements, while by one-electron movements, as in the decomposition of hydrogen peroxide by ferrous iron, oxygen is formed in its ground triplet state (unpublished work).

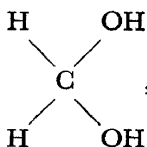
The Trautz-Schorigen luminescent reaction<sup>20</sup> also emits what are probably similar bands<sup>21</sup>. This is a vigorously effervescent reaction between alkaline hydrogen peroxide and formaldehyde to which a polyhydric phenol such as pyrogallol is added. A simple explanation is that the excitation of the oxygen molecule is a spin transfer from a product molecule such as a ketone (K) thermally excited to its triplet state:



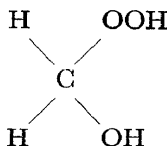
That this is incorrect has been shown by unpublished experiments of Parker, who found no emission when triplet molecules were produced at a high rate in the presence of oxygen by strong irradiation of solutions of benzophenone and of diacetyl.

The Trautz reaction, complex though it is, can at least be partly understood. Formaldehyde and hydrogen peroxide interact to give di-hydroxymethyl peroxide, which decomposes rapidly in strong alkaline solution to formate ions and free hydrogen. A little oxygen is also evolved, but no chemiluminescence is visible. For the Trautz reaction pyrogallol, or some other polyhydric phenol, must be included in the reactants in the proportion of about one mole to ten of the latter. A red glow due to oxygen molecules is then observed, although the proportion of gaseous oxygen in the evolved hydrogen is even smaller than that without pyrogallol addition. The luminescence occurs at the early stages of the reaction only; the pyrogallol is finally completely broken down to simple aliphatic acids, presumably by the Baeyer-Villiger reaction through a quinone as intermediate. No glow is observed if the alkaline solution of pyrogallol is allowed to stand in the air and become oxidized, and it must therefore be associated with a pre-quinone formation stage. Two possibilities have been eliminated by direct experiment. Firstly, the fact that less free oxygen is evolved from mixtures which contain pyrogallol and glow might indicate that high concentrations are unfavourable due to self-quenching. However, reduction of the oxygen concentration in the hydrogen peroxide-hypochlorite reaction by a vacuum or a nitrogen stream had no effect on the glow. A second possibility, that pyrogallol acts as an inhibitor of some fast non-glow reaction, is contradicted by the observation that its addition actually speeds up the over-all chemical change. It then remains to speculate on a likely mechanism by which oxygen molecules of high energy can be evolved, and which accords with the above facts. The following is suggested for discussion.

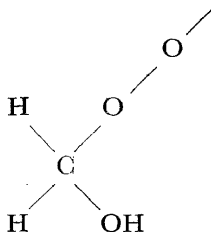
Formaldehyde in aqueous solution exists as



and in presence of hydrogen peroxide could presumably form



Pyrogallol in the oxidizing medium will form a semi-quinone, which may be assumed to produce radicals



by hydrogen abstraction. Two such radicals, probably in their alkaline ionic forms, would yield on collision a molecule of formaldehyde and a formate ion with elimination of an oxygen molecule which could well be electronically excited.

Modern apparatus for detecting light is now sensitive enough to demonstrate luminescence where  $10^{10}$  molecules or more reacting produce only one light quantum, and this field is being studied by several investigators.

A very feeble long-wave emission ( $> 5500 \text{ \AA}$ ) has been observed in the thermal decomposition of organic peroxide solutions, particularly of hydroperoxides<sup>22</sup>, which may also be due to oxygen. Shorter-wave emission from the body of the solution is observed, but the longer-wave component comes from the interface of the vessel in contact with the solution, and is greatly enhanced if the surface has been treated with alkali. The homogeneous thermal decomposition in solution of peroxides such as benzoyl peroxide does not lead to oxygen formation, but in presence of dissolved air peroxy radicals are formed, and these may well evolve oxygen bimolecularly at an alkaline surface and be responsible for the observed chemiluminescence.

Work at very high sensitivities is complicated by the difficulty of eliminating traces of impurities. Light emission has been detected even in simple reactions such as acid-base neutralization, but how far this is an impurity effect is unknown. Temperature radiation from reaction vessels at  $200^\circ$  is

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measurable by a modern photomultiplier sensitive only to visible light. It is found that if the vessel surface is slightly contaminated with organic matter emission can be detected at temperatures as low as 80° in air, but not in an atmosphere of nitrogen. Is this effect incandescence due to the combustion of very small particles of contaminant, or is it luminescence from peroxide decomposition? At this stage of the subject many matters remain highly speculative, but a symposium of this kind is the place for criticisms and further suggestions.

### References

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