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A NEW CHEMILUMINESCENT SYSTEM

Edwin A. Chandross
Bell Telephone Laboratories, Inc.
Murray Hill, New Jersey

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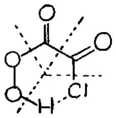
In the course of experiments designed to clarify the nature of some chemiluminescent reactions, we discovered a novel chemiluminescent system. The reaction involved is that of oxalyl chloride and hydrogen peroxide. It can be carried out in either homogeneous solution (aqueous dioxane or dimethylformamide) or two phase mixtures (pentane or benzene and water). The vigorous reaction is weakly chemiluminescent, emitting a bluish-white light. The vapors produced by the reaction have the unusual property of inducing the fluorescence of suitable indicators, e.g., a filter paper impregnated with anthracene. These observations are suggestive of a metastable excited electronic state or some other highly energetic species.

When the reaction is carried out by adding a dioxane solution of the acid chloride (ca. 1M, complexed with dioxane[1]) to a dioxane solution of 30% hydrogen peroxide containing a compound such as anthracene, 9,10-diphenylanthracene or N-methyl acridone (present at ca. 10^{-3}M) it produces a bright chemiluminescence whose color in each case corresponds to the fluorescence of these substances. The presence of alkali has no effect upon this sensitized fluorescence although it does appreciably diminish the evolution of gases capable of exciting the fluorescence of an external indicator.

One might anticipate the following reaction between oxalyl chloride and hydrogen peroxide:

$$H_2O_2 + Cl\text{-}COCOCl \rightarrow HCl + HO_2COCOCl \rightarrow \qquad (1a)$$



I

$$I \rightarrow HCl + 2CO + O_2 \qquad (1b)$$

The analogous simple hydrolysis may be noted here. It is reported to proceed with cleavage of the carbon-carbon bond, yielding only HCl, CO and CO_2.[2] Chromatographic analyses of the nonacidic gaseous products of reaction (1) were performed. The dropwise addition of oxalyl chloride to excess 30% hydrogen peroxide produced considerable amounts of carbon monoxide and oxygen ($CO/O_2 > 2$) as did the reaction of a benzene solution of the chloride with small amounts of 90% hydrogen peroxide. When the reaction was run in dioxane no appreciable amount of oxygen was evolved, probably because of its consumption by radical induced reaction with the solvent. Acetyl chloride, which does not exhibit any luminescent properties under the above conditions, reacts vigorously with 30% hydrogen peroxide but there is no effervescence.

From known thermodynamic data one may estimate that the over-all ΔF for reaction (1) is ca. 70 kcal. per mole. Virtually all of this energy will be liberated in (1b). The possible activation energy for the latter step should also be considered in the light of our mechanism (vide infra). This amount of energy is sufficient to account for visible light, corresponding to one einstein at 408 mμ, but light cannot be emitted during the decomposition of an isolated molecule of I. The energy levels of HCl, CO and CO_2 are too high to permit the formation of one of these species in an excited state. The energy of singlet oxygen, the only possible electronically excited molecule that could be formed from I, is too low (38 kcal.) to account for the observed chemiluminescence. A mechanistic interpretation involving another species is required.

The decomposition of I would involve a change in multiplicity if triplet (ground state) oxygen were formed directly. Unimolecular reactions involving such a change are relatively slow.[3] We propose that fragmentation of I occurs upon collision with another molecule, A, which is capable of accepting electronic energy and undergoing a change in multiplicity:

$$I + A \rightarrow HCl + 2CO + {}^3O_2 + {}^3A^*$$

Thus A catalyzes this reaction and in turn is promoted to a vibrationally excited triplet state (${}^3A^*$). During the loss of vibrational energy this excited molecule can cross over to the potentially fluorescent lowest excited singlet (${}^1A^*$), a process which we feel is important in other chemiluminescent reactions involving oxygen. One might also invoke some sort of delayed fluorescence resulting from thermal activation of the relatively long lived, vibrationally unexcited ${}^3A$ to ${}^1A^*$.[4] However, this is not likely to occur in solutions containing oxygen, an efficient quenching agent for most triplets. Chemiluminescent reactions which require energy transfer, have previously been observed.[5]

It is also possible that unreacted oxalyl chloride might function as the acceptor A. The triplet state of oxalyl chloride has not been studied but one might expect a resemblance to the 1.2-diketones.[6] We have observed bluish-white phosphorescence in frozen (77° K) pentane solutions of the chloride. It is noteworthy that the 1,2-diketones phosphoresce in solution and in the vapor phase. Thus we can explain the observed luminescence in reaction mixtures containing no fluorescent indicator. The oxalyl chloride triplets could also be swept out of the solution by the gaseous reaction products and the presence of such metastable excited molecules may be responsible for the unusual properties of the vapors. The sensitization of fluorescence of an external indicator would then formally require the transfer of energy from a triplet to a singlet, again via the route we have postulated. Although we feel that it is unlikely, the presence of I in these gases cannot be ruled out. The transfer of energy with conservation of spin has been studied for both singlets[7] and triplets[8] but transfer between triplets followed by direct formation of an excited singlet during vibrational decay of the excited triplet has not been proposed. We intend to investigate this possibility in some simple photochemical systems.

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