

CHEMILUMINESCENCE

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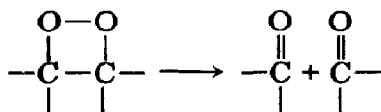
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The emission of light by a chemical reaction has always been a fascinating phenomenon, although it is rarely easy to identify the process yielding the light-emitting species, which is often formed in very small yield. The cool flames observed in the oxidation of many hydrocarbons provide a striking example. Although the complex oscillations which occur in these reactions have been adequately described mathematically and the chemical reactions in question largely identified [1, 2] it is still not known which process yields the electronically excited formaldehyde whose weak emission led to the discovery of these curious oscillations.

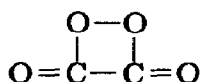
In this short contribution, chemiluminescence will be defined as the formation of excited electronic states in chemical reaction processes, *i.e.* as the inverse of conventional photochemistry. Historically, studies of chemiluminescence began with the observation and description of chemical reactions which emitted light and particularly emphasized the characterization of the emitter involved. The interpretation of the mechanisms of these processes came particularly in the 1960s with the development of new experimental techniques for studying transient species and better theoretical understanding of the potential surfaces and non-adiabatic processes involved.

During that period our knowledge of several types of chemiluminescence developed rapidly. One type was the afterglows [3] which arise from the formation of electronically excited molecules in the recombination of ground state atoms (*e.g.* $N + N$ and $N + O$) or association of other molecular fragments (*e.g.* $O + NO$, $O + SO$ and $H + NO$). A minority of these processes were found to be two-body inverse predissociations directly into emitting states which can be characterized quite precisely. The majority proved to be three-body recombinations into high vibrational levels of molecular ground or excited states from which non-adiabatic transitions (often collision induced) occur to radiating states. For instance, the recombination of ground state nitrogen atoms populates four triplet and two singlet excited states of N_2 with vibrational distributions which depend markedly on the carrier gas used. Because many vibrational levels are populated, sometimes by more than one pathway, these systems are too complex to provide much information on the dynamical behaviour of excited states. These systems have therefore been little studied since the *Journal of Photochemistry* was founded in 1972.

For organic chemiluminescence, the most important development of the 1960s was the application of the Woodward–Hoffmann rules [4] to the decomposition of four-membered rings:



These rules showed that the orbitals in a dioxetane do not correlate adiabatically with those in the ground states of the ketonic products, but correlate with the first excited electronic states of both products. In the decomposition of many dioxetanes, there is a comparatively high probability of forming one electronically excited ketone product by a non-adiabatic path which tunnels through the barrier predicted by the Woodward–Hoffmann rules [5]. Extension of this concept to larger molecules provides a plausible explanation of many bioluminescent processes with their very high luminescence efficiencies [6]. The commercial Cyalume light sources [7] utilize the reaction between an aromatic dioxalate and hydrogen peroxide which is thought to yield a



intermediate that breaks down to give CO_2^* which transfers its excitation energy to an aromatic molecule which fluoresces efficiently. However, the last decade has produced little new evidence on the postulated intermediate.

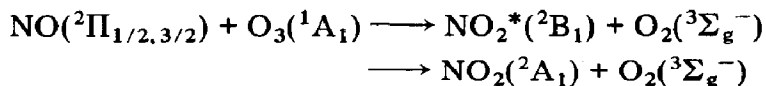
Instead research has concentrated on the use of chemiluminescence as an analytical tool where the high efficiencies achievable in the detection of UV and visible photons give great sensitivity.

This high sensitivity is one reason for the use of chemiluminescence to probe the initial energy distributions of small molecules formed in elementary gas reactions since the emission from relatively few excited molecules is needed to provide vibrational and rotational distributions. Furthermore the shorter radiative lifetime of excited electronic states (about 10^{-7} s) compared with vibrationally excited molecules (about 10^{-2} s) makes it much easier to observe an initial energy distribution under essentially collision-free conditions.

These advantages of chemiluminescence for studying reaction dynamics and the drive to produce chemical lasers in the visible and UV regions have provided the main impetus for the study of chemiluminescent transfer reactions particularly those involving metal atoms over the last decade.

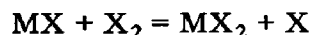
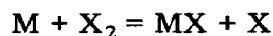
When the *Journal of Photochemistry* was founded, almost the only well-studied transfer reaction yielding electronically excited molecules was that between nitric oxide and ozone. Because it has parallel paths with similar *A* factors but different activation energies to form ground state and electronically excited NO_2 [8] (although the energy distribution in the latter

is not known) the existence of two adiabatic paths provides a good test bed for dynamical studies:

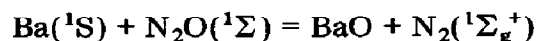


As might be expected vibrational excitation of the ozone [9, 10] is much more effective in promoting reaction than vibrational excitation of the NO [11]. Translational energy is highly effective in accelerating the reaction and there is experimental evidence that the upper spin-orbit component $\text{NO}(^2\Pi_{3/2})$ gives mainly excited NO_2^* whereas $\text{NO}(^2\Pi_{1/2})$ gives largely ground state NO_2 [12]. This would be surprising since the spin-orbit splitting in NO is much less than the translational energies and barrier heights involved. Recent beam studies including variation in the NO rotational energy [13] suggest that the reaction proceeds by abstraction of both the central and the terminal oxygen atoms of ozone. The former path provides a theoretical explanation of the failure to detect electronically excited O_2 as a product [14]. This fascinating reaction will clearly continue to attract attention over the next decade.

The major growth area in gas phase chemiluminescence since 1972 has been the study of the reactions of metal atoms (magnesium, calcium, strontium, barium, aluminium, tin, lead, scandium, lanthanum etc.) with halogens and with N_2O , O_3 , O_2 and NO_2 to yield electronically excited metal halides or oxides. In general, the mechanisms are complex; with halogens, the excited dihalide may be formed by a three-body process or by a double-exchange reaction:



the first reaction providing the source of diatomic MX emission [15]. The formation of diatomic metal oxides often involves a simple transfer reaction, but the best studied of these



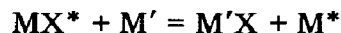
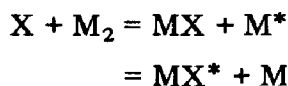
has proved singularly difficult to interpret [16]. Adiabatic correlation rules would lead one to expect the lowest singlet state of BaO to be populated. With increasing internuclear distance, the $\text{A}'^1\Pi$ state crosses the $\text{X}^1\Sigma^+$ ground state at the $\nu = 39$ level of the latter. Thus the $\text{Ba} + \text{N}_2\text{O}$ reaction would be expected to populate the $\text{A}'^1\Pi$ state above this internal energy for BaO and the $\text{X}^1\Sigma^+$ state at lower energies by analogy with the behaviour of CN in flames supported by active nitrogen [17]. However, BaO is formed rotationally hot and this assists collisional mixing of the $\text{X}^1\Sigma^+$ and $\text{A}'^1\Pi$ states with the $\text{A}^1\Sigma^+$ state which emits with a bimodal vibrational distribution. Spin-orbit mixing of the $\text{A}'^1\Pi$ and $\text{b}^3\Pi$ states of BaO further compli-

cates the situation, as does the realization that the ground states of BaO and N₂O do not correlate with ground state dissociation products Ba(¹S) + O(³P) and N₂(¹Σ_g⁺) + O(³P). Therefore, the transition state may well have a low-lying triplet surface and the increase in chemiluminescence yield on exciting a group II element such as magnesium or calcium to its low-lying ³P state [18] supports this view.

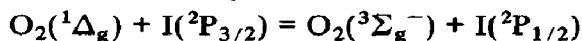
The many studies of such systems have not produced the much-sought chemical laser. One reason is that the reactions populate many vibrational and rotational levels. This and the probable slow depopulation of the lower states make it difficult to obtain the inversion of population needed for laser action to occur. The fascination of many of these systems stems from the unpredictability of the results obtained, an unfortunate reflection of our lack of understanding of the potential surfaces and dynamical processes involved.

A healthier situation is shown by the chemiluminescent reactions between atomic ions (*e.g.* C⁺, N⁺ and O⁺) and small diatomic molecules studied particularly by Ottinger and coworkers [19], which have the advantage that much more is known about the potential energy surfaces involved.

Apart from some beam studies of the classical flame reactions between alkali metals and halogens, which have shown that two parallel paths are important sources of chemiluminescence [15]



the most exciting developments have been in the chemistry of the pseudo-alkali-metal atoms, the ³P metastable states of the noble gases. These show very similar properties to alkali metals having large cross sections for reaction with halogens to give ionic bound excited states of the diatomic noble gas halides [20]. These emit the familiar (but misnamed) excimer laser radiation, which the chemiluminescent reactions of ground state atoms mentioned above have failed to provide. Likewise, the nearest approach to a visible chemical laser ($\lambda = 1.135 \mu\text{m}$) [21] has come from the near-resonant energy transfer process



when oxygen gas which is largely O₂(¹Δ_g) is generated by the liquid phase reaction between alkaline hypochlorite and hydrogen peroxide, which is itself an interesting example of spin conservation.

Future progress in chemiluminescence is highly dependent on a proper understanding of the potential surfaces and the associated non-adiabatic processes involved in the formation of excited species. Because of the computational problems involved, there is much to be said for studying processes involving three or four atoms and only light ones.

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