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Chemiluminescence Excitation Mechanisms

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A systematic review of modern views on the factors which favour the formation of chemical reaction products with greater equilibrium excitation is presented. The excitation can be electronic (for reactions in solution) or electronic and vibrational (for gas-phase reactions). In the latter case, fine details can be revealed, and particular features of the excitation process can be related to the electronic structure of the reactants (atoms or simple molecules). With complex molecules (typical of liquid-phase reactions) only a qualitative or semi-quantitative interpretation is possible. Examples are chosen from among those reactions whose chemiluminescence is adequately understood. Although the excitation mechanism is specific for a particular reaction type, excitation is favoured in general by the participation of ions, radical-ions, and charge-transfer states; these species also favour the retention of the reaction energy as internal energy of the products. 119 references.

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I. INTRODUCTION

The number of papers published on chemiluminescence has been steadily rising during the past few years: new chemiluminescent reactions have been discovered, and new methods of utilising chemiluminescence have been proposed. The rate of publication in the field of chemiluminescence has doubled in 5–6 years, which is higher by a factor of 2–3 than the corresponding figure for scientific information as a whole (doubling every 10–15 years [1,2]).

Papers on chemiluminescence can be divided into several categories, depending on the detail in which the given chemiluminescent system is discussed: 1) initial observations and rough description of the system; 2) identification of the emitter of chemiluminescence and of the chemical steps leading to excitation; 3) quantitative study of the excitation and emission steps.

The present review is devoted to the elementary mechanisms by which chemical energy is converted into light, and will deal mainly with papers in the third category.

II. GENERAL PROBLEMS IN CHEMILUMINESCENCE

A. Definition of Chemiluminescence

The term chemiluminescence usually denotes the emission (in excess of equilibrium) of radiation by particles which have gained excitation in a chemical reaction. If the reaction is split into two stages—the formation of excited particles, and the emission (or quenching) of radiation—it is possible to write a simple relationship between the absolute intensity of chemiluminescence I (in quanta per unit volume and per unit time) and the absolute rate of formation of excited particles w_{P^*} (per unit volume and per unit time):

$$I = \eta_P w_{P^*} \qquad (1)$$

where η_P is the relative probability or quantum yield of light emission by the excited product P^*.

The above definition is too general, and the formula is oversimplified: not surprisingly, therefore, its application in real cases gives rise to difficulties and confusion. We shall consider these difficulties in detail.

1. In keeping with the terminology currently accepted in luminescence, the prefix "chemi" relates to the mode of supply of the excitation energy (cf. photoluminescence, radioluminescence, cathodoluminescence, etc.). Strictly speaking, the name chemiluminescence should be reserved for the emission of light which is observed on mixing reactive materials. However, mixtures of reactants are sometimes chemically inert, and an additional agency is needed to activate them (heat, electrical discharge or electrolysis, illumination). Nevertheless, it is not correct in these cases to talk of thermoluminescence†, electroluminescence, or photoluminescence: the phenomenon should be called chemiluminescence, because the elementary act which gives rise to an excited particle is the chemical reaction between the reactants. In particular, some agencies can give rise to electronically excited particles which react to give an electronically excited product (for example, the reactions of electronically excited $O(^1D)$ and $N(^2D)$ atoms produced by an electrical discharge in the gas): in this case the emission from the product should be classified as chemiluminescence, but the emission from the primary particles is (evidently) not chemiluminescence. In the most recent terminology, the mode of activation or of generation of the reactive particles is also stated (e.g., thermochemiluminescence, electrochemiluminescence, photochemiluminescence).

2. Opinions differ as to the nature (chemical, or physical) of processes such as the transfer of an electron from one particle to another. If the process gives rise to excitation, followed by light emission, we shall term it chemiluminescence only if we take the view that the process itself is chemical. A physical process is sometimes defined as one in which the coordinates of the nuclei

†The term "thermoluminescence" is particularly unfortunate. Literally, it denotes luminescence induced by heating, and some authors actually define it in this way. But this definition is meaningless, since thermal energy by itself cannot give rise to luminescence (i.e. to emission in excess of equilibrium). Thermoluminescence (or thermal de-excitation) is the correct name of an entirely different phenomenon: the emission of light observed on heating solids which have been previously exposed to ionising radiation.

remain unchanged: in this sense, the electron-transfer process is undoubtedly physical. However, the transfer of an electron gives rise to particles with entirely different chemical properties (ions and neutral molecules, or atoms), and there are grounds for treating the process as chemical. In this review, the luminescence arising from processes such as the transfer of an electron from a radical-anion to a radical-cation will be treated as chemiluminescence.

3. In some systems the light is emitted not by the product but by a third particle, excited by energy transferred to it from the excited product. In this case the elementary excitation act is purely physical, but the primary excited particle is formed by a chemical process, and many of the properties of the emission (intensity, time dependence, and spectral composition) are intimately bound up with a chemical mechanism. Hence this type of emission must be classified as chemiluminescence.

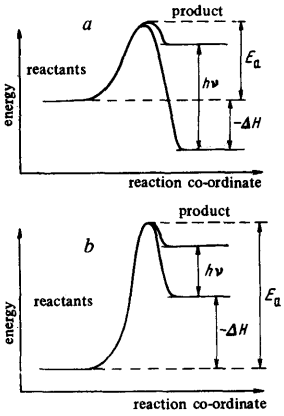


Figure 1. Model of the origin of chemiluminescence in (*a*) exothermic and (*b*) endothermic reactions.

4. Chemiluminescence is not necessarily confined to exothermic reactions. An amount of energy equal to (or not greater than) the sum of the activation energy E_a and the heat of reaction $-\Delta H$ can be converted into excitation energy (Fig. 1). The newly formed reaction products, when chemically activated, contain energy in excess of equilibrium even in the case of endothermic processes. If this excess of energy is lost by radiation, the process is no different from chemiluminescence. Of course, in endothermic reactions rotational and vibrational levels are more likely to be excited than electronic levels, and the radiation will lie in the long-wave (infrared) region of the spectrum.

5. The emission yield η_P is the ratio of the rate of emission (radiative deactivation) from P* to the sum of the rates of all the processes removing P*. The value of η_P for chemical excitation is the same as the emission yield for any other mode of excitation (e.g., photon absorption) under the same conditions (composition, temperature, and other parameters affecting the emission yield). Hence, this quantity is sometimes known from photoluminescence data for the compound P even before the chemiluminescence is measured. However, it is important to remember that the emission yield η_P is equal to the photoluminescence quantum yield only when the same excited state of the particle P is obtained both by chemical excitation and by the absorption of a photon. The situation is illustrated in Fig. 2 for a hypothetical organic molecule. The singlet state S_1 is populated as a result of photoexcitation. If the chemiluminescence is associated with a transition from the singlet state, its emission yield is equal to the photofluorescence quantum yield.

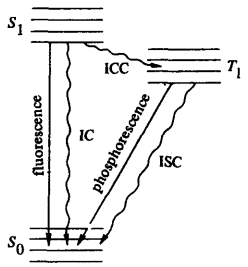


Figure 2. Excited states of a typical organic molecule and optical transitions between states: internal conversion (IC) and intersystem crossing (ISC). *S* and *T* are singlet and triplet states respectively.

However, if a triplet state becomes populated during the chemiluminescent reaction and the emission originates from this state the emission yield becomes equal to the photophosphorescence quantum yield (i.e. the number of quanta of phosphorescence per quantum of light absorbed) divided by the intersystem conversion yield of the triplet state T_1 from the singlet state S_1 (i.e. the ratio of the rate of transitions from S_1 to T_1 to the overall rate of all deactivation paths available to S_1.

In the light of the above, chemiluminescence can be defined as follows: the emission of radiation is termed chemiluminescence if the elementary act by which the emitter is formed consists in a chemical reaction or in the transfer of energy from a chemically excited product formed either spontaneously or as a result of a special energetic interaction.

Chemiluminescence is observed in a particular spectral region if the following conditions apply:

1. The energy of the photon is not less than the sum of the activation energy and the heat of reaction:

$$h\nu \leqslant E_a - \Delta H$$

or

$$\lambda \geqslant 28.6/(E_a - \Delta H)$$

if the wavelength is expressed in μm and the energy in kcal mole^{-1}. (Exceptions to this rule are discussed in section III. A. 5 below.)

2. The lifetime of the excited state of the emitter (with respect to radiation) is small compared to the characteristic relaxation time of the scattering processes for excess energy, or in other words the rate of emission is large compared to the rate of the radiationless deactivation processes, or the emission yield η_P is relatively high.

The overall schemes of chemiluminescence are summarised in Table 1, where the symbol w denotes the total rate of formation of the product P, η_P^{exc} is the excitation efficiency or yield, i.e. the ratio of the number of excited particles to the total number of particles of the same kind produced by the reaction, η_{PA} is the energy transfer efficiency, i.e. the relative contribution of the rate of energy transfer to the overall rate of deactivation of the excited product P*, η_A is the emission yield of the acceptor A, I_P and I_A are the quantum intensities of the emission for the product and the acceptor respectively.

Table 1. Summary of chemiluminescence.

Stage	Particles involved	Rate
Energy interaction	Unreactive components	
	Reactive components	
Chemical reactions	Non-excited product P	$(1-\eta_P^{exc})w$
	Excited product P*	$\eta_P^{exc}\ w$
Physical processes:		
Radiationless deactivation	Non-excited product P	
Emission (chemiluminescence)	Non-excited product and photon $P + h\nu_P$	$\eta_P \eta_P^{exc}\ w = I_P$
Transfer of excitation energy	Non-excited product and excited acceptor $P + A^*$	$\eta_{PA}\eta_P^{exc}\ w$
Emission in the acceptor molecule	Non-excited acceptor and photon $A + h\nu_A$	$\eta_A\eta_{PA}\eta_P^{exc}\ w = I_P$
Deactivation of the acceptor, energy transfer from A* to another acceptor, etc.	Non-excited acceptor and other products	

The proposed scheme leads to the following expression for the total quantum intensity of chemiluminescence I:

$$I = I_P + I_A = (\eta_P\eta_P^{exc} + \eta_A\eta_{PA}\eta_P^{exc})\,w\,. \qquad (2)$$

If energy transfer is negligible, the scheme is simplified and Eqn. (2) reduces to Eqn. (1). However, it may be necessary to consider additional processes, for example parallel reactions giving rise to excited products other than P*, chemical reactions of the excited states leading to new emitters of chemiluminescence, secondary energy transfer from an acceptor A* to another acceptor capable of luminescence, etc. The formula for the intensity then retains the form of Eqn. (2) but becomes more complicated.

B. Chemiluminescence Yield

The most important quantitative parameter of chemiluminescence is the chemiluminescence yield η_{cl}, i.e. the ratio of the absolute chemiluminescence intensity to the rate of the reaction leading to the formation of the excited product‡:

$$\eta_{cl} = I/w\,. \qquad (3)$$

In the light of the above considerations, the chemiluminescence yield is given by the expression in brackets in Eqn. (2):

$$\eta_{cl} = (\eta_P + \eta_A\eta_{PA})\,\eta_P^{exc}\,. \qquad (4)$$

If the scheme is complicated by the presence of additional processes, a more complex expression for the yield is obtained, but in every case it is possible to identify two factors one of which is the excitation yield. These factors have entirely different physical significance, since they stem from different stages in the chemiluminescent process (the chemical excitation stage and the physical energy transfer and emission stage).

We shall not be particularly concerned with the emission stage in the following sections, because light emission from atoms and molecules has been adequately treated in recent monographs [3,4,5], mainly as a result of research on photoluminescence, and also because it tells us very little about the specific features of the chemical excitation mechanism. The excitation stage, on the other hand, will be fully discussed because of the need for quantitative information on the elementary chemical act. This type of information has only just begun to appear in the literature.

In any form of luminescence, the yield reflects the efficiency with which the energy supplied to the system is converted into light. Often the concept of yield is itself far from straightforward, and needs to be discussed specially [6]; this is particularly true of types of luminescence which have not yet been extensively studied (such as chemiluminescence).

It would appear that formula (3) offers a method of determining the yield η_{cl}, but this requires a measurement of the absolute intensity and of the absolute reaction rate. The experimental determination of the intensity involves only practical difficulties (which can, however, be very serious). Much more fundamental difficulties arise in the determination of the reaction rate—we need to know the rate of the particular step which gives rise to excitation. These difficulties become more intractable, the more complicated the reaction. In general, the reaction mechanism must be known, otherwise the problem of measuring the rate of one particular step becomes meaningless. Often, and particularly with complex and with "new" chemiluminescent reactions, the mechanism is not known, and different definitions of the chemiluminescence yield are used in these systems in order to achieve some measure of quantitative description of the phenomenon. For example, the intensity of luminescence is referred to the rate of consumption of one of the reactants, or alternatively the total light emission is referred to the initial concentration. Difficulties in the experimental determination of the yields and in their theoretical interpretation usually arise on going from gas reactions to reactions in a condensed phase, from light particles to polyatomic molecules, and from vibrational to electronic excitation.

‡This quantity is sometimes called the chemiluminescence quantum yield, a term derived from photochemistry and luminescence, where it is used to denote the yield of reaction product or of light per quantum absorbed. In chemiluminescence the relevant concept is the yield of quanta per reacting molecule. Hence it is better to avoid the term "chemiluminescence quantum yield".

III. CHEMICAL EXCITATION MECHANISMS

A. Simple Gas Reactions

In the gas phase the medium has no effect on the various elementary acts, and therefore more reliable and unambiguous information on the chemical reaction mechanism can be obtained. Nevertheless, the theoretical treatment of the excitation act meets with serious difficulties even in the simplest systems.

It is difficult to calculate the reaction rate, and it is even harder to determine to what extent and in what form the energy is concentrated in the products.

1. *Reaction rate*

Consider a simple exchange reaction (Fig. 3)

$$A + BC \rightarrow AB + C \qquad (I)$$

where A, B, and C are atoms. The molecule BC is taken to be immobile in Fig. 3, and is treated as a target for the impinging A atom.

A simple expression for the reaction rate w can be written by making two assumptions:

a) the molecule BC approximates to a sphere of radius b_0; the reaction proceeds with probability $p = 1$ if the atom A (treated as a point) collides with the sphere or approaches it tangentially; if the atom does not touch the sphere, $p = 0$.

b) the velocity of all A atoms is the same.

With these assumptions we can write

$$w = \frac{d[AB]}{dt} = \pi b_0^2 v_A [A][BC] = k[A][BC] \qquad (5)$$

where $k = \pi b_0^2 v_A$ is the rate constant for the reaction, and v_A is the velocity of the A atom.

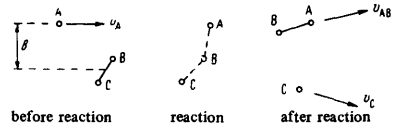


Figure 3. Exchange reaction A + BC → AB + C.

In reality, however, the interaction between the particles BC and A is a function of the distance b, and the reaction probability p (per single collision between A and BC) depends on b, on v_A, and on the internal energy state of the reactants and of the products. Therefore, the cross-section πb_0^2 should be replaced by a cross-section for the reaction from the state n_i for the reactants to the state n_j for the products:

$$\int_0^\infty p(v_A, b, n_i, n_j) 2\pi b db = \sigma_{ij}(v_A, n_i, n_j) \qquad (6)$$

where n_i denotes the quantum numbers corresponding to internal energy states (electronic, vibrational, and rotational) of the initial reactants, and n_j those of the products.

Furthermore, since neither v_A (the relative approach velocity of A and BC) nor the state of internal motion of the reactants is constant, a distribution function for the particles among these parameters must be introduced: $F(v_A, n_i)$. The resulting expression for the rate of production of the product in the quantum state n_j, which is particularly important in chemiluminescence, takes the form

$$\frac{d[AB(n_j)]}{dt} = \sum_{n_i} \int_0^\infty \sigma_{ij} v_A F(v_A, n_i)\, dv_A = w_j \; . \qquad (7)$$

The distribution function F contains the concentrations of the reactants as factors, but (strictly speaking) only in the equilibrium system, and in this case we can write

$$F(v_A, n_i) = f(v_A, n_i)[A][BC] \; . \qquad (8)$$

Equilibrium implies a lack of reaction, and we can dismiss this case as trivial. However, the assumption is often made that the reaction can proceed with very small departures from equilibrium. In this case, inserting Eqn. (8) into Eqn. (7), we obtain the customary rate law for a bimolecular reaction:

$$w_j = k_j[A][BC] \qquad (9)$$

where

$$k_j = \sum_{n_i} \int_0^\infty \sigma_{ij} v_A f(v_A, n_i)\, dv_A \; . \qquad (10)$$

It follows that the rate constant—whose evaluation is the aim of most of the quantitative work in chemical kinetics—is merely an averaged parameter only indirectly related to the real interaction probabilities of the particles and to the mechanism of the reaction.

To a first approximation§, the excitation yield defined above is equal to the ratio

$$\Sigma_2 k_j / \Sigma_1 k_j = \eta_P^{exc} \qquad (11)$$

where the summation 1 is taken over all the states of AB and the summation 2 is taken only over the states which give rise to the experimentally observed chemiluminescent emission.

The exact calculation of the probability p (formula 6) is a quantum-mechanical problem: the result of the interaction between A and BC depends on the properties of the surface (or, more accurately, the hypersurface in multidimensional space) which describes the potential energy for the reaction. The form of the surface must be obtained by a quantum-mechanical calculation. Satisfactory calculations so far have been made[7] only for the simplest of all reactions: $H + H_2 = H_2 + H$.

Evidently, a complete solution of the problem is not likely to be achieved in the near future, even for relatively simple cases and with the approximation discussed above. Nevertheless, we already have interesting examples of partial solutions, which assist in the qualitative interpretation of experimental results for the more complex systems.

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§We ignore the rates at which the given state of the product is populated by internal conversion from other states. Strictly speaking, the right-hand side of Eqn. (9) should then include additional terms of the form

$$\sum_i k_{i_j}[AB(n_i)] - \sum_i k_{j_i}[AB(n_j)] \; .$$

2. *Vibrational excitation in exchange reactions*

Vibrational excitation in exchange reactions has been studied in detail. Reactions of the type

$$H + X_2 \xrightarrow{k_v} HX + X \qquad (II)$$

where X = Cl, Br, or I have been investigated by infrared chemiluminescence [8-13], and reactions of the type

$$M + X_2 \xrightarrow{k_v} MX_v + X \qquad (III)$$

where M = Na, K, Rb, Cs, in crossed molecular beams [14-17]. In these reactions the energy is insufficient to excite the electronic levels of the product. The rate constants k_V describe the population of the rotational states of the v-th vibrational level.

From recent experimental results, and their theoretical treatment, it has been possible to draw various important conclusions regarding the forces between the reactants which eventually lead to the reaction.

It has been shown that in reaction (II) the probability of forming HX in high vibrational states is low. For example, in the case of HCl the following relative rate constants have been obtained for the population of the vibrational states: $k_6 = 0.004$, $k_5 = 0.04$, $k_4 = 0.3$, $k_3 \simeq k_2 \simeq k_1 = 1$. In other words, only a small fraction of the total energy of the reaction (2 eV) is converted into internal energy, whilst the major part is converted into translational energy.

In reaction (III), on the other hand, the greater part of the energy (also ~ 2 eV) is converted into vibration, and the constant k_V is a maximum for the highest possible quantum number v. Furthermore, the cross-section¶ of reaction (III) is significantly higher than the corresponding value for gas-kinetic reactions, and the molecule MX after the reaction tends to move in the same direction as the atom M before the collision.

These features have been successfully correlated with the properties of the potential energy hypersurface. Polanyi and coworkers [10], without attempting to calculate the equation of the hypersurface, took some "ready-made" surfaces, and integrated the classical equations of motion of the atoms A, B, and C for a representative choice of trajectories, allowing for energy and momentum conservation (Monte Carlo method). The form of the surface was found to determine the point at which most of the energy is evolved: whilst the distance between A and B decreases (i.e. during the approach stage—attractive case), whilst the distance between B and C increases (i.e. during the separation stage—repulsive case), or during the transitional phase.

These workers showed that when A is a light atom and B and C are heavy atoms (as in the case of reaction (II)) the proportion of the energy converted into vibrations decreases as the amount evolved during the approach stage decreases, i.e. as the "repulsive" character of the interaction potential increases.

Attraction between the reactants is more characteristic of reaction (III): an electron can be transferred from M to X_2 even at large separations, and the strong coulombic attraction between M^+ and X^-X favours the evolution of reaction energy during the early stages of the reaction, and hence its conversion into vibrational energy. This "harpoon" mechanism is consistent with the ionic character of the M–X bond and with the large cross-section of the reaction. For a particular set of parameters of the reaction system, the theoretical angular distribution of the receding products agrees with that obtained experimentally.

Undoubtedly, the molecular beam method gives a great deal of valuable information about the elementary chemical act, and also in particular on reactions of interest from the standpoint of their chemiluminescence. Unfortunately, the probability of emission during purely vibrational transitions is very low, and existing infrared detectors are too insensitive to reveal the chemiluminescence of the products of reactions (II) and (III) in a molecular beam.

Even in infrared chemiluminescence experiments involving much larger numbers of excited molecules than the molecular beam experiments it is necessary to use large reaction vessels and multiple passes.

The examples considered above are not exhaustive. Vibrational chemiluminescence in exchange reactions has been observed also in the systems H + O_3, H + O_2, H + NOCl, H + NO, etc. In the reaction

$$H + O_3 \rightarrow O_2 + OH; \quad (-\Delta H = 77 \text{ kcal mole}^{-1})$$

(believed to be responsible for the hydroxyl bands in the luminescence of the night sky [17]) the higher vibrational levels of OH (up to $v = 9$) are populated with a higher probability than the lower levels. This is evidence that attraction is predominant in the interaction potential of the reactants [18]. On the other hand, repulsion is predominant in the reaction between N and NO_2 to give N_2O and O. [19]

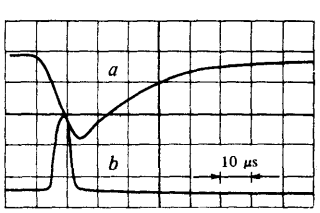


Figure 4. Photolytic pulse (*a*) and laser pulse (*b*) in an F_2O + H_2 chemical laser.

As a result of reaction, some of the sublevels can be more densely populated than sublevels situated at lower energies: in other words, a population inversion is established, and this phenomenon can lead to laser action. Thus, Kasper and Pimentel [20] were able to demonstrate chemical laser action with a mixture of Cl_2 + H_2, using flash photolysis to initiate the chain reaction by decomposing the chlorine molecule into atoms. The spectrum of the laser flash consisted of several narrow lines from vibrational–rotational transitions in the HCl molecule (in the region 3.6–3.8 μm), which appeared sequentially with an interval of the order of microseconds. Other examples of chemical lasers are known: the emission from HF (2.7–3.9 μm), produced by secondary reactions in the flash photolysis of UF_6 with H_2 and hydrocarbons [21,22], and of F_2O

¶The main attraction of the molecular beam method is that the cross sections and the angular distribution of the products (rather than the rate constants) are determined directly. Reactions are therefore characterised in greater details than is possible by conventional gas-kinetic methods.

with hydrogen[23]. The following series of reactions takes place in the UF_6 system:

$$UF_6 + h\nu \rightarrow UF_5 + F,$$
$$F + H_2 \rightarrow H + HF, \quad -\Delta H = 32 \text{ kcal mole}^{-1}$$
$$H + UF_6 \rightarrow UF_5 + HF; \quad -\Delta H = 46 \text{ kcal mole}^{-1}$$

The F_2O system has the advantage that a chain reaction takes place and therefore a single photolytic photon can produce many vibrationally excited molecules of hydrogen fluoride:

$$F_2O + h\nu \rightarrow OF + F,$$
$$F + H_2 \rightarrow HF + H,$$
$$OF + H_2 \rightarrow HOF + H,$$
$$H + F_2O \rightarrow HF + OF.$$

The second and last of the above reactions can excite up to the third and the sixth vibrational level respectively. Laser action is observed as a pulse of radiation (Fig. 4) which is much shorter than the flash of photolytic light.

3. *Electronic excitation of atoms in exchange reactions*

As a rule, excitation in exchange reactions is concentrated on the particle in which a new bond is formed as a result of the reaction. Polanyi and coworkers [12,14] have recently pointed out an exception to this rule: the formation of an electronically excited halogen atom X in reactions of type II:

$$H + X_2 \rightarrow HX + X^*(^2P_{1/2})$$

(X = Br, I), and also, with even higher probability, in the reaction

$$H + HX \rightarrow H_2 + X^*(^2P_{1/2}).$$

The X* atoms are detected by their emission by the forbidden transition $^2P_{1/2} \rightarrow {}^2P_{3/2}$ (10.5 kcal mole^{-1}, 2.7 μm spectral region for the bromine atom).

These processes are much harder to treat theoretically than the processes involving vibrational–rotational excitation. The interpretation involves two potential energy hypersurfaces, one for the electronically excited and one for the non-excited products; at large distances between the reactants these merge into a single surface. The probability of motion of the system over both these surfaces has to be evaluated.

Moulton and Herschbach [25] examined formally analogous reactions (involving also vibrationally excited molecules) in molecular beams. The classical work of Polanyi in the early 1930's had shown (see Ref. 26) that in the chemiluminescent reactions of alkali atoms with halogen molecules the metal atoms are excited by the elementary step (interaction of the metal with the vibrationally excited molecule):

$$M + MX_v \rightarrow MX + M^*.$$

The large cross-sections for this reaction suggest that the interaction is more likely to be chemical ("reactive energy transfer") than a simple vibrational–electronic transfer of energy from MX to M. Moulton and Herschbach gave a direct experimental demonstration of this effect using the "three-beam" method. They observed chemiluminescence from potassium whose electronic levels had been excited by the reactive energy transfer process (V) from the vibrationally excited product of the exchange reaction (IV):

$$\underset{\text{beam 1}}{K} + \underset{\text{beam 2}}{Br_2} \rightarrow KBr_v + Br \qquad \text{(IV)}$$

$$\underset{\text{product beam}}{KBr_v} + \underset{\text{beam 3}}{Na} \rightarrow K^*(^2P) + NaBr. \qquad \text{(V)}$$

The product beam was crossed with a beam of sodium atoms above the photocathode of a photomultiplier with a filter for the 766.5/769.9 nm lines of the radiative transition $^2P \rightarrow {}^2S$ in the potassium atom. The heat of reaction (IV) is 45 kcal mole^{-1}. About one-half of the KBr molecules had an energy in excess of the 41 kcal mole^{-1} needed to excite the K atom in reaction (V) (the energy of the potassium ^2P level plus the difference between the K–Br and Na–Br bond energies). About 40% of these actually followed reaction (V). Because of the high emission probability, the K* atoms were observed within the reaction zone. Thus, one photon was detected for every 5 KBr molecules entering the reaction zone. (The Na atoms were taken in 10^7-fold excess.) From these results Moulton and Herschbach extimate a cross-section of ~ 150 Å^2 for reaction (V)—at least, well in excess of 10 Å^2—i.e. much larger than the gas-kinetic cross-section. This cross-section is larger by an order of magnitude than the cross-section for "non-reactional" transfer, e.g.

$$NaBr_v + K \rightarrow NaBr + K^*$$

which was also investigated by the same authors [25]. These large cross-sections are consistent with the "harpoon" mechanism envisaged for the process.

4. *Electronic excitation of molecules*

Many instances of visible and u.v. chemiluminescence from molecules have been reported in flames, cold flames, and in pre-ignition reactions (see review articles 26–29).

The mechanism of some of these reactions has been studied in fair detail: the rate constants (but not the cross-sections) of the individual steps have been obtained, as well as their temperature coefficients, and a great deal is known about the electronic states of reactants and products, their nature (multiplicity, symmetry type), vibrational–rotational structure, the form of the potential surfaces (or, more accurately, their cross-sections), and the intersections of the different surfaces. It is relatively easy to obtain, experimentally, well resolved chemiluminescence spectra giving valuable information on these reactions.

The adiabatic correlation rules (see Ref. 5, p. 130, and Ref. 26, p. 185) are of the utmost importance in the formation of electronically excited molecules. These rules set stringent limits to the number and the type of electronic states in the products which can be obtained from the states of the initial reactants and which correlate with these states. The formation of excited products often involves a transition to a "forbidden" potential surface at the point where it intersects an "allowed" surface: such a non-adiabatic transition has a low probability.

a. Exchange reactions. Vibrational–rotational excitation is commonest in exchange reactions. However, if the sum of the activation energy and the heat of reaction is greater than the electronic excitation energy of the product, the latter can be produced in an electronically excited state. Of course, this outcome is most likely when the reactants are chemically very active.

Figs. 5 and 6 show the reaction paths for the two bimolecular reactions $NO + O_3 = NO_2 + O_2$ and $SO + O_3 = SO_3 + O_2$: the pre-exponential factors and activation energies are indicated [28]. In spite of their formal similarity, these reactions show some interesting differences. The pre-exponential factors describing the population of the ground

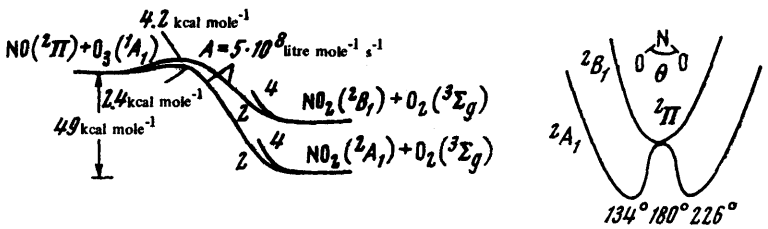


Figure 5. Potential energy diagram for the reaction $NO + O_3 \rightarrow NO_2 + O_2$. The initial state correlates with the doublet but not with the quartet final state.

$^2A_1$ state and the excited $^2B_1$ state of the NO_2 molecule in the reaction $NO + O_3$ have the same value (5×10^8 litre mole^{-1} s^{-1}). On the other hand, in the reaction $SO + O_3$ the ground $^1A_1$ state of the SO_2 molecule is populated with a pre-exponential of 1.5×10^9 litre mole^{-1} s^{-1}, whereas the corresponding values for the excited $^3B_1$ and $^1B_1$ states are 4×10^7 and 1×10^8 respectively. Thrush[28] explains these differences in terms of the adiabatic correlation rules and of the nature of the potential energy surfaces of reactants and products. For $SO + O_3$, one triplet surface for the reactants changes *smoothly* into a triplet surface for the non-excited products of the same symmetry, but it *intersects* two surfaces for the excited products of different symmetry. The probability of reaction to give the excited state is lower, because the probability of the required intersection is low. For the reaction $NO + O_3$, orbital degeneracy (π state) produces two doublet surfaces for the reactants which change *smoothly* into two doublet surfaces for the products.

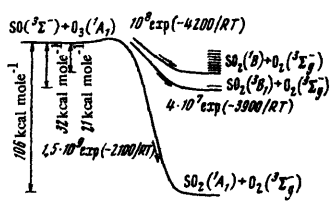


Figure 6. Potential energy diagram for the reaction $SO + O_3 \rightarrow SO_2 + O_2$.

There have been no reports so far of the population of the $^1\Delta g$ (22 kcal mole^{-1}) and the $^1\Sigma g$ (38 kcal mole^{-1}) electronic states of the oxygen molecule in these reactions, although deviations from Wigner's rule can be expected only for reaction paths leading to SO_2 in the $^1A_1$ and $^1B_1$ states. The general rule that excitation is concentrated in the products which contain the newly formed bond may apply also to these reactions.

It is interesting to note that the excited states are populated with high efficiency: although only 70–80% of the reaction energy is converted into electronic excitation, the rate constants are lower than the rate constants for the formation of non-excited molecules by only one to three orders of magnitude. (The excitation energy of NO_2 $^2B_1$ is not accurately known, but it is close to 40 kcal mole^{-1}.)

Like purely vibrational excitation, electronic excitation in exchange reactions gives rise to a non-Boltzmann distribution of the product molecules among the vibrational levels of the upper electronic state. This has been observed, for example, in diffuse flames associated with the reaction of alkali metal vapours with halogenomethanes[30–32]. The emitter of chemiluminescence in these reactions, C_2 in the $A^3\pi_g$ state (55.4 kcal mole^{-1} above the $^3\pi_u$ ground state), is excited during the elementary act

$$C + CX \rightarrow C_2 + X.$$

Table 2. Vibrational levels v' whose population $N(v')$ is a maximum, and relative population $N(v')/N(0)$ of the vibrational levels of the electronically excited $A^3\Pi$ state of the C_2 radical (produced in the reaction between potassium vapour and halogenated methanes).

Halogenated methanes	$CHCl_3$	CCl_4	CBr_4	CI_4
Energy of the C–X* bond, kcal mole^{-1}	77	77	66	50
v'	2	6	1	3
$N(v')/N(0)$	2	55	2	17

*Estimated by Miller and Palmer[31] with an accuracy of 4 kcal mole^{-1}. The uncertainty in these values may be even greater, because the initial data[31] were later shown[32] to be doubtful. However, we may assume that the relative magnitudes of the bond energy are correct.

A definite correlation has been reported[30,31] between the exothermicity of the elementary act, i.e. the energy of the C–X bond, and the energy of the vibrational level which is populated with the highest probability. However, recent work[32] at low pressures and high spectral resolution does not confirm this conclusion. Hence, the maxima in the distribution of the product over the vibrational levels cannot be directly related to the exothermicity of the reaction (see Table 2), and the large difference between the K + $CHCl_3$ and K + CCl_4 systems shows that the assumption of a common mechanism for the formation of the emitter for all reactions of a given type is an oversimplification.

b. Addition reactions. Practically all the known chemiluminescent reactions are termolecular:

$$A + B + M \rightarrow AB^* + M \qquad (VI)$$

The third body M disposes of some of the energy and thus prevents the immediate decomposition of the newly formed AB molecule. Reaction (VI) can follow several paths and lead to different states of the product AB. If A and B are free atoms, the high degree of degeneracy can lead to correlation between the initial state and a number of stable states of the product (see, for example Fig. 7). The chemiluminescence is not necessarily emitted from these states: their potential energy surfaces may intersect other surfaces, and transitions to new states can take place.

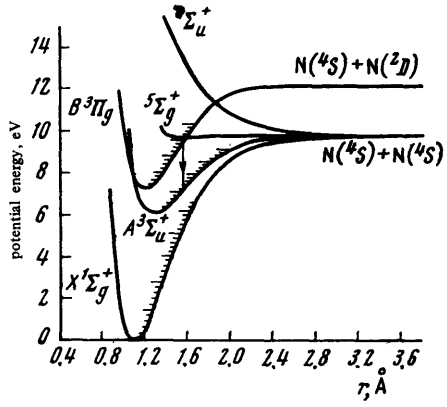


Figure 7. Potential energy curves for the nitrogen molecule.

The yellow "afterglow" of nitrogen in an electrical discharge is an example of chemiluminescence of this type: the emission comes from electronically excited N_2 molecules produced by the recombination of N atoms. Emission occurs after transition of the nitrogen molecule from the states $A^3\Sigma_u^+$ and $^5\Sigma_g^+$ to the state $B^3\Pi_g$, which correlates with a state of the free atoms in which one of them is excited[29].

The third body M also can act as the emitter of chemiluminescence, particularly if it is a metal atom with a low excitation potential, e.g.[33-35]

$$H + H + Na \rightarrow H_2 + Na^* \quad (590\ nm)$$
$$H + H + Tl \rightarrow H_2 + Tl^* \quad (535\ nm)$$
$$H + OH + Pb \rightarrow H_2O + Pb^* \quad (406\ nm)$$
$$H + X + Pb \rightarrow HX + Pb^*$$

(where X is a halogen atom). In the reaction

$$O + O + O \rightarrow O_2 + O(^1S)$$

one of the oxygen atoms acts as the third body, by accepting some of the energy of the reaction (5.1 eV) and going into a ^1S excited state (4.17 eV). This process can occur only at very low pressures, and it has been detected (postulated. Sci. Ed.) in the upper atmosphere. The well known "green atmospheric line" at 557.7 nm is due to the transition of an O atom from a ^1S level to another (also excited ^1D level located 1.96 eV above the ^3P ground state[17,36,37].

Other examples of chemiluminescent addition reactions include NO + O + M ("air afterglow"), N + O + M, H + NO + M, O + SO + M, O + CO + M, O + H + M, and others.

None of these gas-phase chemiluminescent reactions has been investigated as extensively as the air afterglow reaction. But even the latter has not yet been fully interpreted: clearly, its mechanism is very complex. The main difficulty is to account, at the same time, for the influence of the nature of the third body M on the luminescence intensity and for the independence of the luminescence intensity on the concentration of M over a wide range of pressures.

Many workers[38-40] have treated the reaction of NO and O as a bimolecular radiative association, but most workers now incline to the view that this reaction is termolecular (see discussion in Ref. 41); it has also been suggested that vibrational relaxation[42,43] (energy redistribution) and redissociation by collision[43] of the electronically excited nitrogen dioxide play a significant role.

Under some experimental conditions the well known tendency of NO to associate may be important. When the gas is allowed to expand adiabatically into a low-pressure chamber, the equilibrium

$$n\,NO \rightleftharpoons (NO)_n$$

is shifted towards the right by the cooling effect[44]. Most of the associated species are dimeric, but clusters with a mass number up to 600 have been detected mass spectrometrically[45]. Excitation is more likely in the reaction $(NO)_n + O \rightarrow NO_2^* + (NO)_{n-1}$ than with the monomer; in the case of the dimer, between 1 and 10 collisions of the dimer with an oxygen atom are needed[45] to form an electronically excited NO_2^* molecule. This explains the anomalously high (by 3–4 orders of magnitude) chemiluminescence intensity of nitric oxide in the upper atmosphere[46,47]. Under normal (non-adiabatic) conditions the excitation probability is low (of the order of 10^{-5} excited molecules[41] per collision between NO and O). However, the probability of the overall reaction $NO + O \rightarrow NO_2$ is also of the same order, and therefore not less than one-half of the molecules of product are formed via an electronically excited state[48], and most of the collisions do not lead to a reaction.

The great importance of chemiluminescent reactions stems from that fact that they occur both in artificial and in natural processes. Many reactive particles are formed in the upper atmosphere under the influence of u.v. radiation from the sun. Their chemiluminescence provides information on the composition of the atmosphere, on the movement of air masses, and on solar activity. An interesting new method of investigation is the slow release of an active material from a rising rocket, and observation of the bright chemiluminescence produced by the reaction between this material (nitric oxide, triethylboron, trimethylaluminium, sodium or aluminium vapour) and atoms present in the atmosphere[46,47,49]. "Air afterglow" is observed in the wake of bodies moving at supersonic speeds: atoms and radicals are produced by thermal dissociation of the oxygen in the compressed layers of air ahead of the moving body, and the resulting chemiluminescence gives information on the streamline properties of the body, on the transition from laminar to turbulent flow, etc.[50,51] Lastly, observations of chemiluminescence can lead to numerical values of chemical bond energies, rate constants, and to spectroscopic information on the structure of molecules and radicals[27].

5. *Excitation of singlet oxygen*

The chemical excitation of molecular oxygen calls for a special discussion, because it has recently been shown to

play an important role in some liquid-phase chemiluminescent reactions as well as in the gas phase.

O atoms can be produced by an electrical discharge in O_2. Under favourable conditions up to 10% of the O_2 molecules formed by recombination are obtained in the $^1\Delta_g$ state, and up to 0.1% in the $^1\Sigma_g^+$ state [52]. Emission from singlet states is both spin- and parity-forbidden and has a very low probability. For example, the radiative life time τ_0 for the magnetic-dipole $^1\Delta \rightarrow {}^3\Sigma$ transition (1270 nm band) is 5.3×10^3 s.

It has recently been shown [52-54] that, in addition to isolated singlet molecules, double molecules as a collision pair (but not forming a complex) are able to emit light. Careful study of the emission spectra has revealed bands corresponding to transitions between vibrational sublevels of the electronic states of O_2 molecules and O_4 dimers (Fig. 8).

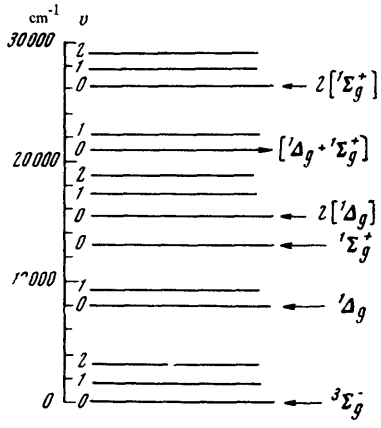


Figure 8. Electronic states of oxygen molecules and dimers [55]. Some vibrational levels are indicated.

The intensity of emission at 634 nm, corresponding to the $^1\Delta {}^1\Delta \rightarrow {}^3\Sigma {}^3\Sigma$ transition, is proportional to the square of the concentration of singlet molecules

$$I_{634} = k[O_2{}^1\Delta]^2$$

where $k = 0.28$ litre mole^{-1} s^{-1}. [54] (According to Falick and Mahan [56], this constant has the value 0.03 litre mole^{-1} s^{-1}.) From the scheme

$$2O_2{}^1\Delta \underset{k_3}{\overset{k_1}{\rightleftharpoons}} (O_2{}^1\Delta)_2 \xrightarrow{k_2} (O_2{}^3\Sigma)_2 + h\nu \qquad \text{(VII)}$$

we easily obtain formula (7), with $k = k_1k_3/k_2$. Hence, taking $k_1 = 10^{11}$ litre mole^{-1} s^{-1} and $k_2 = 10^{13}$ s^{-1}, we obtain $k_3 = 28$ s^{-1}, or $1/k_3 = 3.6 \times 10^{-2}$ s for the lifetime of the radiation, which is 5 orders of magnitude shorter than for the transition in an isolated molecule. Since the pair $O_2^*O_2^*$ exists only as a collision state, $1/k_2 \simeq 10^{-13}$ s, and only one collision between excited oxygen molecules in $k_2/k_3 \simeq 10^{11}$ leads to emission. The $O_2{}^1\Delta$ molecule is fairly stable: collisional deactivation by oxygen and nitrogen molecules occurs with rate constants of 10^3 and 10^1 litre mole^{-1} s^{-1} respectively [57]. Hence, only one in 10^8 collisions between singlet and non-excited O_2 molecules causes deactivation of $O_2{}^1\Delta$, and the concentration of singlet oxygen can reach relatively high values. From the ratio of the emission intensities from dimeric and monomeric O_2 molecules

$$\frac{I_{634}}{I_{1270}} = \frac{k[O_2{}^1\Delta]^2}{\tau_0^{-1}[O_2{}^1\Delta]} = k\tau_0[O_2{}^1\Delta] \qquad (12)$$

combined with the above values of k and τ_0, we conclude that the ratio becomes greater than unity when the pressure of singlet oxygen exceeds a few tens of mmHg. In low-pressure experiments the quantum intensity of the 634 nm emission is always lower than the quantum intensity of the 1270 nm emission, but the former is easier to detect because photoelectric cells are much more sensitive in the visible than in the infrared region.

Evidently, this emission mechanism allows the photon energy to be much greater than the energy evolved in the elementary chemical act. This is the exception to the rule outlined at the beginning of this article.

B. Reactions in the Liquid Phase (Electronic Excitation)

The quantitative study of the elementary excitation acts in solutions is very much harder than the study of chemiluminescent gas-phase reactions.

Most liquid-phase reactions involve polyatomic molecules. The quantum-mechanical description of polyatomic molecules relies on approximate computational methods, in which the transition from the simplest one-electron system to more complex systems is made by various means. There is no exact theory of the elementary act in condensed systems. Neither the transition state theory nor the collision theory is able, in practice, to predict reaction rates from the structure of the reacting species. A direct calculation of the motion of the representative point of the system along the potential energy surface, such as has been done for the $H + H_2 \rightarrow H_2 + H$ reaction, is impossible in a more complicated system. The same is true of an exact calculation of the influence of the solvent.

Most chemiluminescent liquid-phase reactions in solutions are complicated processes involving many intermediate steps whose mechanism is as yet far from clear. Both the reactions themselves and their chemiluminescence are characterised by complex kinetics, and quantitative data on chemiluminescence and excitation yields are very difficult to obtain.

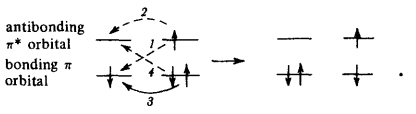
For this reason, the standards and the criteria used in liquid-phase chemiluminescence studies are quite different from those used in gas-phase systems. Workers studying simple gas reactions aim to understand every detail of their mechanism—a realistic albeit laborious objective. On the other hand, with the complex molecules involved in liquid-phase reactions one must be content with a simple, qualitative interpretation. Workers rely heavily on analogies: on the one hand, with the simpler gas-phase systems, on the other hand with photochemical and photophysical processes. (Note that chemiluminescence is "photochemistry in reverse".)

Relatively few of the steadily increasing number of papers on liquid-phase chemiluminescence have attempted to study the phenomenon in reactions where the mechanism is known. However, a number of well chosen model systems have been described in recent years, and several types of excitation mechanism have been shown to have wide application. We shall consider a few examples of these mechanisms below. A more detailed description of the specific features of chemiluminescence in solutions can be found in various reviews [57-66] and in Gundermann's monograph [67].

1. *Electron transfer*

Consider the transfer of an electron from an anion-radical M^- (or $^2M^-$, where the left-hand superscript denotes the multiplicity) to a cation-radical A^+ (or $^2A^+$). A^+ has a deficiency of one electron with respect to the molecule A, and M^- has one electron in excess; the last bonding orbital and the first antibonding orbital are filled, as shown below:

$$^2A^+ + {}^2M^- \longrightarrow {}^1A + {}^1M^* \qquad \text{(VIII)}$$



The transition can occur in several ways. Transition *1* gives only non-excited products (not shown). However, if the excitation potential of at least one of the product molecules is less than the difference between the ionisation potential and the electron affinity (or, if M^- and A^+ have the same solvation energy, less than the difference between the oxidation and the reduction potential), it is possible to obtain an excited and a non-excited molecule (path *2* and path *3*, the latter shown in the diagram), or even two electronically excited molecules (path *4*)†.

Excitation by the mechanism of radical-cation and radical-anion annihilation was first demonstrated by Chandross and Sonntag [68]. These workers observed singlet–singlet emission from 9,10-diphenylanthracene (DPA) during the reaction between potassium diphenylanthracene (source of DPA^-) and the 9,10 dichloride of DPA (source of DPA^{2+}). Weller and Zachariasse [69] observed chemiluminescence during the reaction of the anion-radicals (M^-) of chrysene, picene, pyrene, 1,2-benzanthracene, anthracene, perylene, and tetracene with the cation of Würster Blue (D^+). Chemiluminescence had been predicted by the authors before the experiment: since the fluorescent state of the aromatic hydrocarbons M* is quenched by electron donors D through the formation of a charge-transfer complex M^-D^+, the authors suggest that the opposite process—the interaction of M^- and D^+—can lead to chemical excitation.

The electrochemical production of ion-radicals is an effective way of studying the chemiluminescence associated with electron transfer. Chemiluminescence accompanying electrolysis has been reported by several workers (see review in Ref. 65), but the recent work by Hercules [70] on the chemiluminescent annihilation of aromatic ion-radicals has produced a veritable avalanche of reports of electrochemiluminescence. Electrochemical excitation using a.c. is particularly revealing, because both cations and anions are produced at any one site of the layer adjacent to the electrode during each half cycle (by the reactions $M + e^- \rightarrow M^-$, $M \rightarrow M^+ + e^-$, and $M^- \rightarrow M^+ + 2e^-$). The electrochemiluminescence is particularly intense if the voltage applied to the electrodes is sufficient to produce both types of ion-radical. When one type only is produced, the observed chemiluminescence is weaker by several orders of magnitude. The mechanism of this "pre-annihilation" [71] electrochemiluminescence is still unclear (see discussion in Ref. 72), and so are also many other features of the phenomenon such as the roles of the solvent, of impurities, of the products, etc. (see discussion of Hoytink's paper at a Discussion of the Faraday Society [73]).

†For examples, see Fig. 9 below.

Hoytink [73] summarises current views on the thermodynamics and kinetics of electrochemiluminescence by discussing the annihilation of the radical-ions of aromatic hydrocarbons (M). The heat of reaction ΔH does not differ significantly from the difference between the oxidation and the reduction potential of M, which are themselves close to the oxidation and the reduction half-wave potential respectively. It is evident from Table 3 that the exothermicity is sufficient to populate the triplet states, and in some cases also the singlet excited states. The formation of either state during reaction is determined by the relative rates, which can be assessed by considering the intersection of the potential energy surfaces (where the initial and the final state have the same nuclear conformation). The energy change accompanying electron transfer depends mainly on the change in the orientation of the solvent: according to Marcus' theory [74], this change can be characterised by the average distribution of the electron (m) between the participants to the reaction. For example, for the initial state $M^+ + M^-$ the energy minimum corresponds to $m = 0$, whereas for the final state M + M, to $m = 1$. The energy change is proportional to m^2, i.e. it has a parabolic form, which differs for the various combinations of states of the products (singlets, triplets, excimers). The position of the parabolas (Fig. 9) for strongly exothermic reactions shows that the energy barriers separating the initial state ($M^+ + M^-$) from the electronically excited products (curves *3* and *4*) are much lower than the barrier between the initial reactants and the non-excited products (curve *2*). Hence, excitation occurs with 100% probability at the intersection points (to the approximation of the statistical spin factor). On the other hand, the rate of formation of the non-excited product is low, because of tunnelling transition is required (the intersection point is not reached in practice). This transition is similar to the transition involved in the internal conversion from the S_1 state to the S_0 state (see Ref. 4, p. 82–84).

Table 3. Energy balance during cation–anion annihilation [73].

Hydrocarbon	Half-wave potential, V		$-\Delta H$, eV	Energy, eV	
	oxidation	reduction		singlet	triplet
Benzene	2.26	(—3.16)	5.4	4.7	3.6
Naphthalene	1.57	—2.60	4.2	3.9	2.6
Phenanthrene	1.49	—2.48	4.0	3.6	2.7
Pyrene	1.14	—2.10	3.2	3.3	2.1
Anthracene	1.10	—1.98	3.1	3.3	1.8
Perylene	(0.77)	—1.67	2.4	2.9	—
Tetracene	0.80	—1.58	2.4	2.6	1.3

This phenomenon has a clear physical meaning. The elementary act of electron transfer does not involve a change in the nuclear coordinates: therefore, it is fast, and the slower processes of energy dissipation among the bonds cannot compete with the faster processes in which the reaction energy is set free in the form of electronic excitation energy [68]. A somewhat different explanation can also be given [75]: when the product is formed in the ground state the whole of the (electronic!) energy of the reaction must be converted into vibrational energy. This process has a low probability, as shown by the low rate

constant for the internal conversion illustrated in Fig. 2 (of the order of 10^5 s^{-1}). On the other hand, when the electronically excited state is populated the greater part of the electronic energy of the reaction is converted into electronic energy of the product.

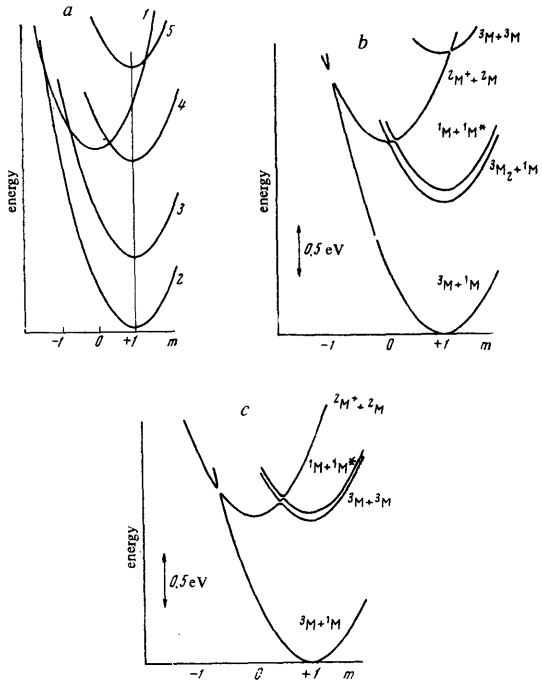


Figure 9. Potential energy curves for a typical radical-ion annihilation (*a*) and for the annihilation of naphthalene (*b*) and tetracene (*c*) radical-ions. Figs. *b* and *c* show the non-intersection ("repulsion") of the curves. *1*) Initial state, *2*) non-excited products, *3–5*) electronically excited products.

As regards the emission stage, we can say the following. The life time of the triplets (^3M) is large, and in liquids these species are effectively quenched. Hence, their contribution to the electrochemiluminescence results from triplet–triplet annihilation, yielding a singlet excited molecule $^1M^*$:

$$^3M + {}^3M \rightarrow {}^1M^* + {}^1M\,.$$

Direct emission from the triplet state has a low intensity in solutions, although in principle it can be enhanced by exchange interaction between the triplet molecule and radical-ions or other triplet molecules. The main contribution to the electrochemiluminescence comes from directly excited singlets ($^1M^*$) and singlet excimers ($^1M_2^*$). The electrochemiluminescence spectrum is qualitatively similar to the photofluorescence spectrum [76], but the relative importance of monomers and excimers is different in these two different types of excitation.

It is evident from Fig. 9 that the barrier to the reverse reactions of the type

$$^3M + {}^3M \rightarrow M^- + M^+$$

can be relatively low. Processes of this type have been observed in the photoexcitation of fluorescein [77], eosin [78], and Methylene Blue [79].

The rapid progress made in the study of electrochemiluminescence is largely due to the practical advantages of the method: the particles whose interaction produces the elementary excitation act can be prepared at a known and controllable rate.

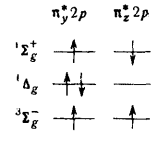
Electrochemiluminescence can be characterised by its yield, defined as the average number of photons emitted per electron transferred from one electrode to the other [71]. Its value can be calculated from the absolute luminescence intensity and the electrolysis current. For example, in the electrolysis of *N*-methyl-1,3-di-*p*-anisyl-4,7-diphenylisoindole in dimethylformamide solution the emission amounts to 3×10^{-3} photon per electron. Allowing for the fluorescence yield, this is equivalent to 0.6% conversion of the electrical energy into excitation.

2. *Excitation of molecular oxygen*

The formation of singlet oxygen molecules in liquid-phase as well as in gas-phase reactions has recently been demonstrated. For example, when a stream of molecular chlorine is passed through an alkaline aqueous solution of hydrogen peroxide, oxygen in the $^1\Delta$ state is obtained in at least 10% yield [80]. The chemiluminescence of reactions of this type has been successfully investigated, mainly because the emitter is a simple molecule in which the nature and the energetics of the excited states are well known. The electronic configuration of the O_2 molecule is obtained by combination of the atomic orbitals of the O atoms:

$$2O\,(1s^2 2s^2 2p^4) \rightarrow O_2\,(KK\,(\sigma 2s)^2\,(\sigma^* 2s)^2\,(\sigma 2p)^2\,(\pi_y 2p)^2\,(\pi_z 2p)^2\,(\pi_y^* 2p)\,(\pi_z^* 2p));\ {}^3\Sigma_g^-.$$

Thus, we obtain eight bonding and four antibonding orbitals, and the bond order is two. The nature of the $^3\Sigma$, $^1\Delta$, and $^1\Sigma$ states is determined by the occupancy of the upper antibonding orbitals [81]:



(IX)

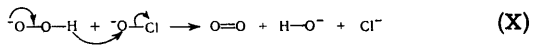
In the $^1\Sigma$ state the unpaired electrons reside in different orbitals, spatially distinct, and this state (like the $^3\Sigma$ ground state) can be thought to have the properties of a biradical ($^{\cdot}O–O^{\cdot}$). On the other hand, in the $^1\Delta$ state the two electrons occupy the same antibonding orbital, while the other orbital remains empty: this structure is similar to that of ethylene (O=O). [82] These differences are responsible, on the one hand, for the different reactivities of the three states of molecular oxygen and their participation in reactions of different types [83]. (For example, the $^1\Delta$ state does not react [84] with NO, NO_2, and H_2O_2 whereas the $^1\Sigma$ state is effectively quenched by water [53].) On the other hand, it has been suggested that the different states of O_2 are produced in reactions of different types [82].

According to McKeown and Waters [82], the production of "biradical" oxygen is most likely in one-electron elementary acts involving free radicals, for example

$$[Fe(CN)_6]^{3-} + {}^{\cdot}O–OH \rightarrow [Fe(CN)_6]^{4-} + {}^{\cdot}O–O^{\cdot} + H^+.$$

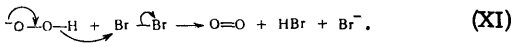
The formation of "ethylene-like" singlet oxygen is more likely in heterolytic reactions, i.e. in elementary acts

involving the participation of electron pairs, as in the reaction between H_2O_2 and alkaline hypochlorite solutions:



(X)

or in the reaction between H_2O_2 and halogens:



(XI)

As in the case of gas-phase reactions, the emission spectra of liquid-phase reactions contain bands due to both free molecules and dimers of oxygen.

It follows from Eqn. (12) that the ratio of the photocurrents at 634 and 1270 nm in the chemiluminescence spectrum is proportional to the concentration of singlet oxygen:

$$i_{634}/i_{1270} = a[O_2^1\Delta] \qquad (13)$$

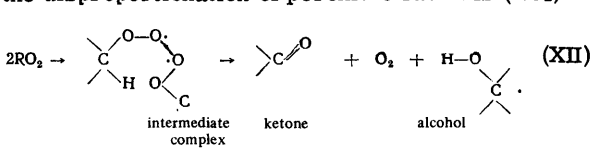
where a is a coefficient depending on the spectral sensitivity of the detector but independent of the geometry of the apparatus and of quenching by collisions. This coefficient can be evaluated by calibrating the apparatus for the 1270 and 634 nm bands using an electrical discharge in gaseous O_2. Hence, the concentration of singlet oxygen and the yield (10%) of $O_2{}^1\Delta$ in the reaction between hydrogen peroxide and chlorine can be determined experimentally[80]. It should be noted, however, that in this liquid-phase reaction the emission occurs from the gas bubbles (chlorine) rising through the solution. In these circumstances the fate of the singlet O_2 molecules is determined by the same rate constants as in the gas-phase reaction (section III.5). The rate constants of processes involving singlet oxygen as a true solute have not yet been measured.

The discovery of chemiluminescence was responsible for the interest in the problem of singlet oxygen and its participation in physical, chemical, and biological processes‡.

The "double" energy of the dimers (from 45 kcal mole^{-1} for $^1\Delta^1\Delta$ to 75 kcal mole^{-1} for $^1\Sigma^1\Sigma$) can facilitate reactions with a large activation energy. Khan and Kasha[55] attempted to formulate a general theory of chemiluminescence in reactions leading to the production of singlet oxygen. They assume that the emitter can be either the O_2O_2 pair or an acceptor species carrying the energy of the excited dimer. However, they were unable to produce a quantitative proof of these views: undoubtedly, this is because the kinetics and the mechanism of the overall reaction are complex, and the elementary excitation act cannot be isolated for study.

3. *Excitation of carbonyl compounds during the oxidation of organic materials*

The oxidation of organic compounds in solution by molecular oxygen is often accompanied by weak chemiluminescence[60,61,88]. Excitation occurs in one of the elementary steps of the complex chain reaction involved: during the disproportionation of peroxidic radicals (RO_2):



(XII)

The emitter of chemiluminescence in the visible region of the spectrum is a ketone in the triplet state.

This reaction can be studied conveniently because its rate w, and therefore also the chemiluminescence intensity I (see Eqn. 2), can be controlled by adding chain oxidation initiators (peroxides or azo compounds). In the presence of strongly luminescent energy acceptors A, formula (2) applies exactly, and the emission yield η_P of the ketone can be determined by varying the concentration of A (and thus varying the efficiency η_{PA} of the energy transfer). The low value of η_P (10^{-5}–10^{-3}) is due to the low probability of triplet–singlet emission and to strong deactivation by molecular collisions with the solvent. The excitation yields can be evaluated by formula (2) once the absolute chemiluminescence intensity I, the rate w, and the yield η_P are known. The values 10^{-3}–10^{-2} were obtained[89,90] for the excitation yield of ketones (acetophenone, cyclohexanone, benzophenone, diacetyl) in the oxidation of the hydrocarbons ethylbenzene, cyclohexane, diphenylmethane, and ethyl methyl ketone respectively.

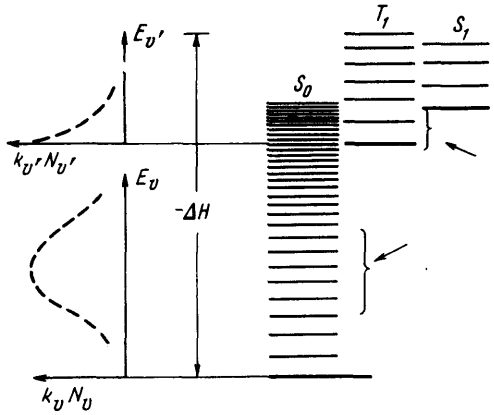


Figure 10. Population of the energy states of a ketone during the disproportionation of peroxide radicals. Probable energy dependences of the rate at which the vibrational levels are populated are shown on the left for the S_0 and T_1 electronic states. The arrows denote the levels with the highest occupancy probability.

Hence, the excitation yields are fairly large, considering that an energy of between 55 and 75 kcal mole^{-1} (depending on the structure), or 60–70% of the heat of reaction (XII), needs to be concentrated on the ketone (one of the three products) in order to excite it. The quantity η_P^{exc} can be treated[88,90] as the ratio of the rates at which the S_0 and T_1 states of the ketone are populated (Fig. 10):

$$\eta_P^{exc} = \left(\sum_{v'=0}^{\infty} k_{v'}N_{v'}\right) \Big/ \left(\sum_{v=0}^{\infty} k_vN_v\right)$$

where $k_{V'}$ and k_V are the rate constants which describe the population of the vibrational levels of the T_1 and S_0 states respectively, and N_V is the number of configurations of the intermediate complex for which the ketone molecule acquires an energy equal to the energy of the vibrational

‡These problems attracted lively discussion in the literature of the 1930's and 1940's (see Section 79 and others in Terenin's monograph[3]). More recent reviews can be found in Refs. 85–87.

level v (or v'). Using rate constants averaged over the number of configurations, we arrive at

$$\eta_P^{exc} = (\bar{k}_{v'}/\bar{k}_v)\left(\sum_{v'=0}^{\infty} N_{v'}\right)\Big/\left(\sum_{v=0}^{\infty} N_v\right) = \frac{k_{v'}}{\bar{k}_v} n_T$$

where n_T denotes the fractional number of the states of the intermediate complex for which the energy acquired by the ketone is at least equal to the energy of the triplet state of the ketone. This fraction is evidently very small, since electronic excitation of the ketone requires much more than half the energy of reaction (XII). Yet, the low value of n_T is compensated by the ratio $\bar{k}_{V'}/k_V$; there are grounds for expecting this ratio to be much larger than unity:

1. The energy of the reaction is, essentially, electronic, since the rearrangement of the intermediate complex to give the final products involves a change in the electronic structure of the given combination of atoms. Studies of the radiationless deactivation of electronically excited organic molecules have shown that Franck–Condon factors play an important role in the conversion of electronic energy into vibrational energy. These factors inhibit the conversion to an extent which varies inversely with the energy (see Section 4–3 of Ref. 4). The rate constants $k_{V'}$ and k_V relate, on the average, to processes in which a small and a large fraction respectively of the energy of the reaction are converted into vibrations (Fig. 10).

2. If we accept the analogy with gas-phase exchange reactions (Section III.A.2), and assume that the bonds formed in reaction (XII) are not ionic, and are more similar to those of reaction (II) than to those of reaction (III), we again conclude that the conversion of a large fraction of the energy of reaction (XII) into vibrational energy has a low probability, and hence its rate constant is low.

3. Lastly, as was stated above (Section III.B.1), the high yields of electrochemiluminescence are due to the fact that the conversion of large amounts of electronic energy into vibrational energy is unnecessary.

The low occupation probabilities of the upper vibrational levels of the electronic ground state indicate that in the overwhelming majority of elementary acts of type (XII), when the energy acquired by the ketone is insufficient to cause electronic excitation, the reaction does not take place and the peroxide radicals simply separate after an encounter. This may be one of the reasons why the absolute rate constant for the disproportionation of peroxide radicals is much lower than the rate constant for diffusion, even though the radicals experience tens or even hundreds of collisions at each encounter, and the activation energy for disproportionation is equal to the activation energy for diffusion.

It should be noted that detailed studies of chemiluminescence have been made only on hydrocarbons whose oxidation involves secondary peroxide radicals, so that disproportionation takes place in a six-membered complex (reaction XII). With tertiary radicals this complex cannot form, and chain termination is brought about by the reactions

$$2ROO^{\cdot} \rightarrow ROOOOR \begin{cases} \nearrow ROOR + O_2 \\ \searrow 2RO^{\cdot} + O_2 \end{cases} . \qquad (XIII)$$

In the oxidation of cumene, for example, the oxy-radical can dissociate as follows:

$$C_6H_5{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}{-}O^{\cdot} \rightarrow C_6H_5{-}\overset{\displaystyle CH_3}{\overset{|}{C}}{=}O + \dot{C}H_3 .$$

This reaction is exothermic by about 10 kcal mole^{-1}, and the suggestion [91] that it is the source of excitation of acetophenone at 150° is clearly untenable. In this temperature region the decomposition products of tertiary peroxides have been shown to contain ethers, whose presence is ascribed [92] to the disproportionation of oxy-radicals e.g.

$$2\,(CH_3)_3CO^{\cdot} \rightarrow (CH_3)_2C{=}O + CH_3{-}O{-}C\,(CH_3)_3 .$$

If a reaction of this type is possible in the case of cumyl oxy-radicals, it may indeed give rise to excitation of acetophenone, since its enthalpy change is at least 80 kcal mole^{-1}.

Alternative excitation mechanisms are suggested in the current literature for the chemiluminescence of oxidation reactions. Bowen and Lloyd [93–95] and Reich and Stivala [96] assume that the ketone is excited by the molecular decomposition of a hydroperoxide (a reaction product):

$$-\overset{|}{\underset{H}{C}}{-}O{-}O{-}H \rightarrow -C{=}O + H_2O; \quad -\Delta H = 70\text{–}80 \text{ kcal mole}^{-1}. \qquad (XIV)$$

Reaction (XIV) has a relatively large activation energy, and could be significant at high temperatures. However, there is no direct proof that it takes place as a single elementary act [97]. Many peroxides decompose by a radical mechanism rather than by the molecular mechanism (XIV):

$$-\overset{\diagdown}{\underset{H}{C}}{-}O{-}O{-}H \rightarrow -\overset{\diagdown}{\underset{H}{C}}{-}O^{\cdot} + {}^{\cdot}OH; \quad \Delta H = 35 \text{ kcal mole}^{-1}.$$

Disproportionation of the radicals produced by this reaction gives the same final products as reaction (XIV):

$$-\overset{|}{\underset{H}{C}}{-}O^{\cdot} + {}^{\cdot}OH \rightarrow -C{=}O + H_2O; \; -\Delta H = 110 \text{ kcal mole}^{-1}.$$

The radicals can also behave as oxidation initiators, and the observed chemiluminescence could simply be the result of the disproportionation of peroxide radicals.

Two more mechanisms are noteworthy. Stauff and coworkers [98] described the reaction

$$2RO_2 \rightarrow R_2 + O_2^{*}{-}O_2^{*} \qquad (XV)$$

and Lloyd [95] postulated the reaction

$$ROOH \rightarrow RH + O_2^{*} \qquad (XVI)$$

as paths for the formation of singlet oxygen. Unfortunately, no evidence whatever is quoted of the reality of these processes. It is hard to believe that deeply oxygenated compounds can lose the whole of their oxygen in elementary processes of the type of (XV) or (XVI). Reaction (XVI) could conceivably take place at high temperatures and in the presence of a powerful catalyst, but not on a glass wall at 80°.

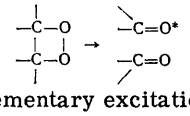
Partial excitation of molecular oxygen in reactions of type (XII) has been proposed [60,61], and more recently Howard and Ingold [99] have confirmed this view by a chemical argument. The initial spin state in reactions (XII) and (XIII) is singlet or triplet (combination of two doublet states of free radicals), and the spin conservation rule predicts the formation of products in both the singlet and the triplet state, although the final system is profoundly affected by the energy distribution factors.

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In spite of the uncertainties still present in chemiluminescence problems, particularly as regards liquid-phase reactions, there are indications that the generality

(or, conversely, the specificity) of the factors leading to efficient excitation in various reactions will become better understood during the next few years. We may assume that one of these factors will be shown to be the participation of ions, radical-ions, or charge-transfer complexes: as the data discussed in this review suggest, these species favour the retention of the reaction energy as internal energy of the products.

Whilst this paper was in press, new calculations of the energy distribution of the products of exchange reactions have been published [100,101], and also a review [102] and new work on chemical lasers including the first report of purely chemical laser action [103,104] and of continuously operating chemical lasers [105,106]. Luminescence of nitrogen dioxide has been observed in crossed molecular beams [107]. In addition to the fully characterised electronic and vibrational excitation, chemical reactions can also generate non-equilibrium occupancy of nuclear spin states: studies of chemical pumping of this type were started [108] in 1967 and are attracting considerable attention at the moment [109]. Many of the recent results point to the decomposition of a cyclic peroxide group, e.g.



as the commonest elementary excitation act in liquid-phase chemiluminescence.

A process of this type is characteristic of the chemiluminescence produced by the oxidation of the light-emitting substance found in the firefly and its analogues (e.g. lophine), [110-114] of organic anhydrides and amides [115] (in this case the strongly fluorescent molecule acts as "catalyst" and as emitter by gaining electronic energy from the products which are not amenable to excitation), and other reactions. The high excitation efficiency accompanying the decomposition of the peroxide ring follows from the rule of orbital symmetry conservation [116]. Different views on the mechanism of the chemiluminescence attending the oxidation of organic compounds have been critically discussed [117], and Kellogg [118] comes to the surprising conclusion that the excitation yield of the ketone approaches 100%, with quenching by oxygen retained in the solvent cage. Interesting new data are presented in a review of the physical aspects of chemiluminescence [119].

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