CHEMILUMINESCENCE IN SOLUTIONS

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I. INTRODUCTION

CHEMILUMINESCENCE is one of the least investigated forms of luminescence. "From the energy point of view", S. I. Vavilov wrote in 1932, "there is no doubt that the excitation of molecules or atoms accompanied by chemiluminescence is obtained at the expense of the liberated chemical energy, but in no case is the mechanism of the excitation of chemiluminescence known reliably." [5b]

Has the position changed since this was written? In the last 20—30 years, much progress has been made in the investigation of chemiluminescence in gaseous reactions, thanks to the work of V. N. Kondrat'ev, A. N. Terenin, M. Polanyi, and others.* The luminescence mechanism in liquid-state reactions has been investigated much less. However, interest in this subject has recently increased greatly because weak luminescence has been found in a wide variety of biological and chemical systems.
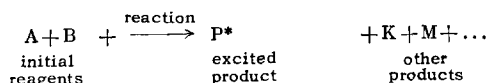
The purpose of the present paper is to review the current state of investigations of the mechanism of chemiluminescence and to consider the probable development of this area of chemical physics. The review deals with liquid systems but other forms of chemiluminescence are also briefly discussed.

1. General Relationships Governing the Effects

Chemiluminescence represents superequilibrium radiation, whose brightness exceeds the brightness of thermal radiation. Departures from equilibrium are caused by chemical reactions.

The process of chemiluminescence can be divided into two stages:

1) Excitation stage: the formation, in a chemical reaction, of an energy-rich particle (reaction product P) in a state (P*) from which radiative transition is possible:

$$A+B + \xrightarrow{\text{reaction}} P^* +K+M+\cdots$$

$$\text{initial reagents} \qquad \text{excited product} \qquad \text{other products}$$

*Investigations of the luminescence of gaseous reactions, in particular, flames, represent a large part of chemical physics with clearly formulated basic principles, rich experimental material, and important practical applications. [32,49,50,115] Discussion of chemiluminescence in the gaseous state is outside the scope of the present review but we shall quote examples of such luminescence in order to clarify a number of basic characteristics of chemiluminescence.

2) Luminescence stage:
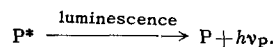
$$P^* \xrightarrow{\text{luminescence}} P + h\nu_P.$$

The experimentally determined quantities—the intensity of luminescence and the reaction rate—are related by

$$I = \eta_P \eta_P^{\text{exc}} w; \tag{1}$$

here, the reaction rate w is the number of molecules of the product formed per unit time in unit volume; the excitation quantum yield η_P^{exc} is the ratio of the number of excited molecules of the product to the total number of molecules formed; the quantum yield of luminescence η_P is the ratio of the number of molecules P*, which give up their energy in the form of radiation, to the total number of excited molecules; the intensity of chemiluminescence I is the number of photons emitted per unit time from unit volume of the reacting mixture.

The total chemiluminescence yield $\eta_{cl} = \eta_P \eta_P^{\text{exc}}$ for various reactions spans many orders of magnitude: from several per cent (few reactions) down to $10^{-8} - 10^{-10}$ and even 10^{-15}.

The low chemiluminescence yields are not surprising and we can understand them as part of the general nature of the effect. Chemiluminescence is a nonequilibrium process. In the chemical reaction zone, energy-rich reaction products are rapidly deactivated. The opposite process—accumulation of the energy of several elementary acts in one particle—is unlikely (particularly in the liquid phase). The energy received in the excitation stage may be numerically equal to the sum of the thermal yield and the reaction activation energy (Fig. 1); therefore, chemiluminescence should be observed in that spectral region which corresponds to the excitation energy or at longer wavelengths.

The limitations imposed by the law of conservation of energy are not the only restrictions on chemiluminescent reactions. Elementary chemical reactions should satisfy the law of conservation of the multiplet state of a system (Wigner's rule), which can be formulated as follows: if the initial and final states of a system do not have the same values of the total spin quantum number, transitions between such states are very unlikely; these transitions should be dominated by other elementary processes, in which the resultant spins in the initial and final states are equal. [50,115] A change in the total spin may be one of the reasons for the low yield of chemiluminescence.
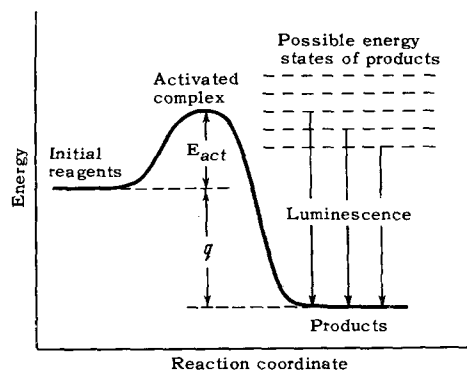
FIG. 1. Schematic representation of the generation of lumine-scence in an exothermal reaction. E_{act} is the activation energy; q is the thermal effect.

Another reason for this low yield may be the competition of other processes with the luminescence of an excited molecule: deactivation by quenching substances, transfer of energy, and internal deactivation. These processes tend to establish equilibrium with the surrounding medium. Equilibrium is not established at once and not equally rapidly for all the degrees of freedom. In general, the electronic and rotational temperatures are different and higher than the experimental temperature, although the distribution may be of the Boltzmann type for each of the forms of motion.

These features of chemiluminescence appear particularly clearly in gaseous reactions. For example, in the exothermal reactions

$$H + Cl_2 \rightarrow HCl + Cl,$$
$$H + NOCl \rightarrow HCl + NO$$
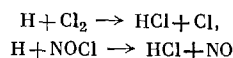
we observe infrared chemiluminescence, corresponding to transitions between the vibrational levels of HCl. The distribution of the ground electron state levels of HCl is of the Boltzmann type at a pressure of 0.2 mm Hg,[92] but at 10^{-2} mm Hg the distribution is far from the Boltzmann type.[93] It is found that the various vibrational states are formed at very different rates and the lower the level, the higher the rate. Collisions equalize the distribution and make it of the Boltzmann type. This explains an experimental observation which at first seems very strange: at high pressures, the higher vibrational levels (up to v = 9) are filled, while at low pressures, the lower levels (only up to v = 4) are filled.

In this example, the exchange of the vibrational energy in collisions is more rapid than the transformation of the vibrational into the translational and rotational energies. Therefore, the total amount of the vibrational energy decreases little during the excited-state lifetime, and at 0.2 mm Hg the vibrational temperature is found to be 2700°K; consequently, the brightness of chemiluminescence is greater than the equilibrium value.

In the liquid phase, because of the high frequency of collisions, the vibrational excitation is lost very rapidly

and the rotational structure is absent. This is probably why no purely vibrational transitions have yet been found in the chemiluminescence of solutions, and in those cases when the chemiluminescence spectra have been obtained and interpreted they have been found to be electronic emission spectra of the reaction products (see below).

Thus, chemiluminescence is a fairly complex phenomenon, which is governed, on the one hand, by the kinetics and mechanism of a chemical reaction, and, on the other, by the luminescence and secondary physical processes in which excited molecules participate.

These problems involve, respectively, a part of chemical kinetics and the science of luminescence. In order to investigate the relationships governing chemiluminescence, which is frequently very weak, we must have sensitive optical apparatus.

2. Short Historical Outline

Chemical kinetics and luminescence are young sciences, formulated in the second quarter of the twentieth century. The same is true of the techniques of optical measurement—convenient and sensitive detectors and recording circuits have been developed only in the last decade.

It is not, therefore, surprising that considerable progress in the investigation of chemiluminescence has been made only recently, although the study of this subject has a long history extending over many centuries; we shall consider now this history briefly (cf. also [63,103]).

Chemiluminescence of living organisms or bioluminescence (luminescence of fishes, worms, insects, mollusks, fungi, rotting wood) has much attracted the attention of scientists—even in antiquity. The first references to bioluminescence are found in Aristotle, and more detailed descriptions were given by Pliny the Elder.

Scientists in the Middle Ages were also very curious about bioluminescence. This is not surprising since they were especially interested in its practical applications: light sources for the illumination of streets, ships, and, particularly, gunpowder magazines (for safety reasons!). They attempted to find such methods of conserving living organisms so as to be able to excite their luminescence at any given moment. They were not successful.

The first to approach the problem scientifically was Robert Boyle. He was the first to establish the stimulating effect of oxygen on chemiluminescence and reached the stage of identifying bioluminescence as an effect accompanying the process of slow oxidation. Boyle investigated in detail the luminescence of phosphorous. This investigation should be regarded as the first work on chemiluminescence: before that, only the luminescence of living organisms or substances derived from them were investigated.

In the eighteenth and nineteenth centuries, chemiluminescence was studied to some degree by many scientists, including Réaumur, Davy, Peltier, Becquerel, V. V. Petrov, Dewar, and, at the beginning of the twentieth century, by Trautz, P. P. Shorygin, Harvey, and Lommel.

By the 1930's, a large number of substances were known to give relatively bright luminescence in certain reactions, mainly oxidations by strong oxidants and by oxygen itself. The strong brightness of the luminescence in these reactions is related either to a high reaction rate or to a high yield. Obviously, such conditions are not satisfied in reactions taking place at moderate temperatures (slow rates), and in reactions resulting in products incapable of luminescing efficiently (low yield). Therefore, one would expect that many reactions to be accompanied by low-intensity chemiluminescence.

The problem of the widespread occurrence of chemiluminescence arose every time when new experimental methods were introduced. At the beginning of the twentieth century, Trautz and Shorygin[151,152] published a long paper in which they listed a large number of reactions of inorganic and organic compounds, accompanied by chemiluminescence; the luminescence was observed with an adapted eye. The photographic method* was then introduced into chemiluminescence investigations but it was applied to reactions accompanied by fairly bright luminescence.

Further confirmation of the widespread occurrence of chemiluminescence was obtained by René Audubert and his colleagues,[55,80,81] who detected, using Geiger-Müller counters, exceptionally weak ultraviolet luminescence from many reactions.

In the late thirties, Audubert stopped investigating chemiluminescence. One of his last papers on the subject ended with the words: "In the present state of exceptionally unfavorable and technically difficult methods, it is not surprising that the number of results obtained so far is small. However, success with the photoelectric counter technique should, it is hoped, make it possible to use widely a method which has already given such very interesting results."[55]

Photomultipliers have become widely available in recent years. The application of these devices has made it possible to detect immediately luminescence in many chemical reactions. Such investigations were begun in 1958 at the Chemical Physics Institute of the U.S.S.R. Academy of Sciences,[7] and in 1960-1962, in Canada,[108] Sweden,[76] U.S.A.,[78] and Western Germany.[142]

Visible luminescence has been recorded in the following reactions:

1) ozonization of hydrocarbons;[6]

2) thermal decomposition of peroxides, hydroperoxides, and azocompounds in solutions;[7]

3) thermal decomposition and oxidation, in the gaseous phase, of peroxides, hydroperoxides, alkyl iodides, alkyl nitrites, nitric acid, nitromethane, acetalaldehyde,[10,71] ethylhyponitrite;[108]

4) electrolysis of ethanol, acetic acid, potassium acetate,[10,71] sodium salts of acetic, propionic, citric, and tartaric acids, Grignard reagents, aminoacids, and many other organic substances;[76]

5) oxidation, by oxygen itself, of hydrocarbons and other organic compounds in solutions;[11,43]

6) condensation of acid chlorides with amines, poly-condensation (reaction producing nylon);[73]

7) destruction of polypropylene and other polymers by oxidation;[79,134]

8) oxidation of urea by hypohalites,[142] etc.

Thus, chemiluminescence is found in a large number of reactions of very different classes and types. Since luminescence has been observed in industrially important reactions (oxidation, decomposition, poly-condensation), it is, in principle, possible to use the photoelectric measurement of chemiluminescence to develop methods of continuous automatic control and regulation of chemical engineering processes.[72]

II. MECHANISM OF CHEMILUMINESCENCE

3. Oxidation of Luminol and Similar Compounds

Albrecht[77], in 1928, first observed the bright luminescence of luminol.

The chemiluminescence of luminol and similar compounds is usually investigated in a complex mixture consisting of water (solvent), potassium and sodium oxide hydrates, hydrogen peroxide, hydrazide, and an "activating agent": a strong oxidant of the sodium hypochlorite type, or potassium ferricyanide, or a metal of variable valence.[62,63]

Diacetylhydrazine, $-O=NH-NH=O-$, is a group capable of such reactions. Substituents in positions 3 and 4 do not take part in the reaction; they affect mainly the luminescence stage, as indicated by approximately the same reactivity of many hydrazides which differ very strongly in the brightness of their luminescence.[57b,96,158]

The luminescence of this system is enhanced by the addition of substances decomposing into free radicals (initiators).[87] Conversely, the introduction of compounds which capture radicals (inhibitors) weakens chemiluminescence.[87,141,149,153] These observations indicate the participation of free radicals in such reactions. From this point of view, a luminescence catalyst should help in the decomposition of hydrogen peroxide or some intermediate reagent into radicals. A. K. Babko[1,2] has used a physicochemical analysis method to show that luminol forms complexes with catalysts (copper salts) and that these complexes are the active components of the excitation process since they emit

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*One of the first to use the photographic method was A. A. Grinberg, [35] who investigated the oxidation of pyrogallol.
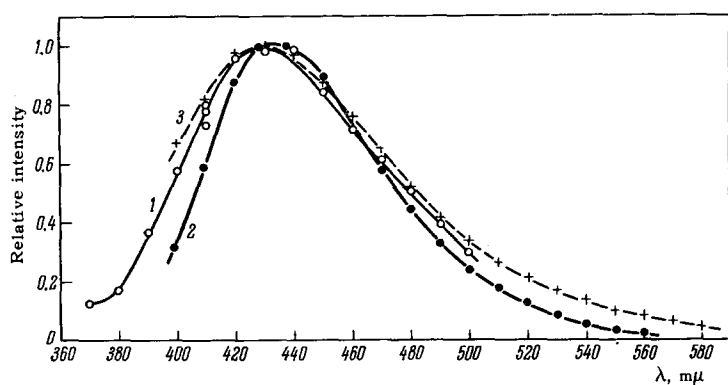
FIG. 2. Chemiluminescence spectrum of luminol in an alkaline medium (1); fluorescence spectra of luminol in an acid medium (2) and of aminophthalic acid in an alkaline medium (3).

much more light when they react with H_2O_2 than does luminol itself. Copper is an unusual catalyst: having once taken part in the oxidation process, it is no longer active in the reaction (probably it forms a complex with oxidation products). Investigations of chemiluminescence are very difficult because of the complexity of the chemical mechanism.

Nevertheless, important data on the mechanism of the luminescence of luminol have been obtained in the last few years.

Again Seliger[138] carried out a careful comparison of the yields and of the chemiluminescence and fluorescence spectra of individual components of the system. He obtained the following results.

1) The maximum chemiluminescence yield (for pH 11) is 0.02 photons per oxidized molecule of luminol.

2) The chemiluminescence yield depends on pH in the same way as the fluorescence yield of 3-aminophthalic acid, but differently from the fluorescence yield of luminol.

3) The fluorescence spectrum of the acid is identical with its chemiluminescence spectrum. The fluorescence spectrum of luminol is also identical with its chemiluminescence spectrum (Fig. 2).

These and many other results indicate that aminophthalic acid is an emitter of chemiluminescence.

Recently, White[154-156] has shown that, in strongly polar but weakly acid solvents (for example, dimethylsulfoxide and dimethylformamide), only luminol, oxygen, and a base are needed for luminescence. The brightness in dimethylsulfoxide is considerably higher than in water (quantum yield ≈ 0.1). The relative simplicity of the chemical system has made it possible to investigate the reaction and luminescence mechanisms. Nitrogen and aminophthalate ions (up to 90%) are among the products. Obviously, the latter is a product of the stage in which energy is liberated and the excitation takes place. The whole chemiluminescence mechanism of luminol can be represented, according to White, by the following scheme:
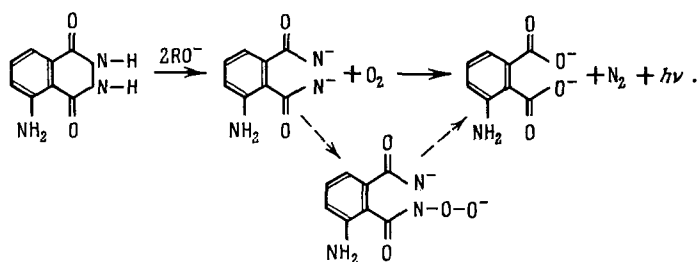

The dashed arrows show a possible different reaction—through the formation of an intermediate hydroperoxide ion. The energy yield of the reaction is approximately 90 kcal/mole. The exothermal nature of the reaction is associated mainly with the formation of nitrogen molecules and, therefore, the emitter is most likely to be excited in the stage of nitrogen formation. From this point of view, the excitation very probably takes place in the reaction of the phthalate ion.

The conclusions of Seliger and White have been confirmed recently in a study of the chemiluminescence of luminol, stimulated by electrolysis.[114]

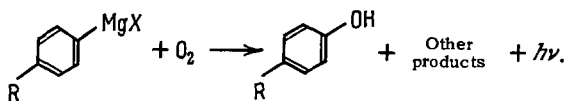Other strongly luminescent reactions have been investigated much less than the oxidation of luminol.

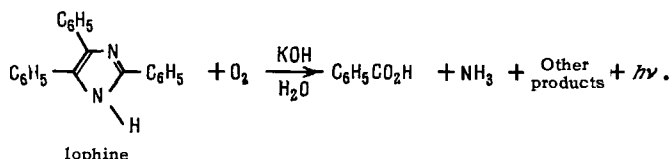The most probable scheme of the oxidation of lucigenin is as follows:[154]

N-methylacridone
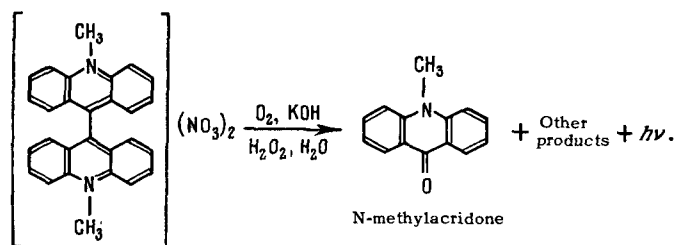
A. V. Karyakin[48] has shown that the chemiluminescence spectra of lucigenin and some of its analogs are identical with their phosphorescence spectra and, con-

sequently, the triplet states of molecules may be excited.

The high intensity of the chemiluminescence accompanying the oxidation of Grignard reagents is solely due to the high reaction rates; the yield is low and amounts to only about 10^{-8} photons/molecule. The reactions take place at the same rate at $+17$ and $-40°C$ and are probably governed by the rate of diffusion of O_2.[87] The whole chemiluminescence scheme can be represented as follows:[14]

$$\text{(structure) } \underset{R}{\overset{MgX}{\diagup}} + O_2 \longrightarrow \underset{R}{\overset{OH}{\diagup}} + \underset{products}{Other} + h\nu.$$

The following scheme has been proposed for the oxidation of lophine (2,4,5-triphenylimidazole) with hydrogen peroxide[154]

$$C_6H_5 \overset{C_6H_5}{\underset{H}{\diagdown}} C_6H_5 + O_2 \xrightarrow[H_2O]{KOH} C_6H_5CO_2H + NH_3 + \underset{products}{Other} + h\nu.$$

lophine

Recently, however, the application of the EPR and spectroscopic methods, as well as the detection of nitroso compounds, has shown that, in this reaction, a free radical 2,4,5-triphenylimidazile is formed:[104]

$$C_6H_5 \overset{C_6H_5}{\diagdown} C_6H_5.$$
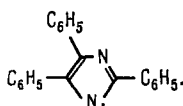
Similar data have been obtained for the chemiluminescence of 2,3,4,5-tetraphenylpyrrole, a substance whose structure is similar to that of lophine.[104] It is possible that the luminescence in these reactions is due to peroxides, which are products of the interaction between radicals and oxygen. A clear correlation between chemiluminescence and chemical activity has been demonstrated for 14 derivatives of lophine: the logarithm of the relative intensity is linearly related to the Hammett sigma-parameter, which represents the reactivity.[126]

The chemiluminescence observed in the oxidation, by hydrogen peroxide, of an alkaline solution of pyrogallol $C_6H_3(OH)_3$ is concentrated in a narrow band near 630 mμ.[86] This is obviously the radiation of a complex of two O_2 molecules in the $^1\Delta_g$ states (cf. Sec. 6). The chemiluminescence of pyrogallol is enhanced by the enzyme peroxidase.[123]

A bluish-white chemiluminescence accompanies the oxidation of oxalyl chloride with hydrogen peroxide:[91]

$$ClCOCOCl + H_2O_2 \longrightarrow HCl + HO_2COCOCl \longrightarrow 2HCl + 2CO + O_2.$$
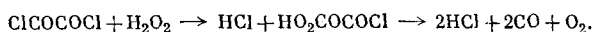
The thermal yield of the reaction (70 kcal/mole) is sufficient for luminescence in the visible region, but none of the products has suitable excited levels. It is possible that the emitter is a third particle to which

energy is transferred; such a particle may be, for example, unreacted oxalyl chloride.

4. Thermal Decomposition

In 1958, luminescence was observed in the decomposition of peroxides, hydroperoxides, and azocompounds in solutions at 50—100°C.[7]

This chemiluminescence was extremely weak and to measure it a very sensitive photometric apparatus was assembled.[9] Further improvement in the method led to the development of the apparatus shown in Fig. 3, which was used also in the investigation of the oxidation hydrocarbons (cf. Sec. 5).

The reaction is carried out in a container C, heated with water from a thermostat. The chemiluminescent light travels along a light guide (a polished glass or quartz block) LG and falls on a photomultiplier PM_1. The photocurrent is amplified and recorded automatically. To record the luminescence spectrum, the light is passed through a large-aperture spectrometer and collected by a collector lens CL and another light guide LG, whence it passes to the photocathode of a photomultiplier PM_2. The scanning is achieved by the rotation of a diffraction grating DG. The apparatus can be used also to record the photoluminescence spectra. For this purpose, the container C is illuminated through a light filter LF from a mercury lamp L. A replica of a diffraction grating, measuring 150 × 140 mm and with 600 lines/mm, is used in the spectrometer.[17] The focal length of the spherical mirror objective is 300 mm, the aperture ratio 1 : 1.5, and the height of the slits 70 mm. Because the slits are curved, the spectrometer can resolve, for a slit width of 0.5 mm (spectral slit width 1 mμ), lines separated by 2 mμ. The high sensitivity of the photomultipliers is achieved by the suitable selection and cooling to $-(50-60)°C$. Under the most favorable conditions, the sensitivity to the total radiation (without decomposition into a spectrum) amounts to 50 photons/sec incident on the
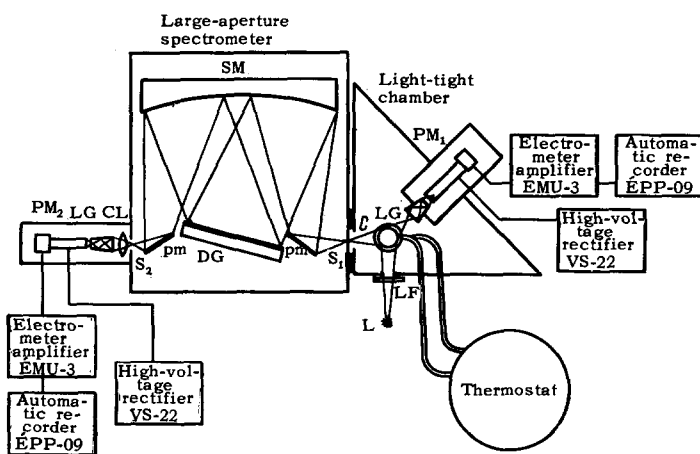

FIG. 3. Schemantic diagram of apparatus used to investigate chemiluminescence.
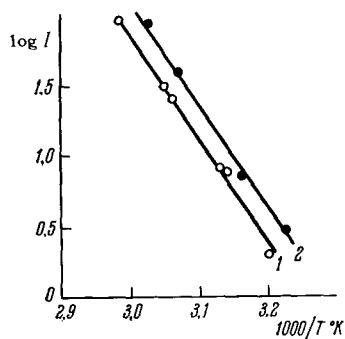
FIG. 4. Dependence of the logarithm of the intensity of luminescence on the reciprocal of temperature in the decomposition of azobisisobutyronitrile in ethylbenzene (1) and of diacetyl-peroxide in chlorobenzene (2).

photocathode surface for an amplifier time constant of 20—30 sec.

In the thermal decomposition, the chemiluminescence is concentrated in the blue part of the spectrum. The intensity is proportional to the concentration of the decomposing substance and increases with temperature in accordance with the law

$$I \sim \exp\left(-\frac{E}{RT}\right) \qquad (2)$$

(Fig. 4), where the parameter E is identical with the activation energy of decomposition of the investigated compounds.[7,10,73] These features indicate that the excitation takes place during the recombination of radicals. In fact, the first act in the decomposition of peroxides, hydroperoxides, and azocompounds is the breaking of bonds.

The radicals which are then formed may take part in further reactions, resulting in new products and radicals. Under these conditions, pair collisions of radicals are unavoidable and these give rise to the recombination. Such processes liberate considerable energy (90—120 kcal/mole), equivalent to quanta in the visible part of the spectrum.

Under steady-state conditions (radicals are not accumulated), the rate of recombination of radicals w_{rec} is equal to their rate of formation

$$w_{rec} = w_i. \qquad (3)$$

The radicals appear in the thermal decomposition of a substance Y at a rate

$$w_i = 2f_c k_0 [Y], \qquad (4)$$

where k_0 is the decomposition rate constant; f_0 is the efficiency, allowing for the possibility of the recombination of radicals just formed ("coefficient for emergence from a cell"); the multiplier 2 takes account of the fact that the dissociation of one molecule produces two radicals. Since the excitation takes place during the recombination of radicals, the intensity of chemiluminescence is proportional to the rate of this process [cf. Eq. (1)]:

$$I = \eta_{cl} w_{rec}. \qquad (5)$$

It follows from Eqs. (3)—(5) that the intensity is proportional to [Y]:

$$I = 2\eta_{cl} f_c k_0 [Y]. \qquad (5')$$

Moreover, the constant k_0 can be written in the form of a product of a pre-exponential term a_0 and an exponential term $\exp(-E/RT)$. Hence, we obtain immediately the temperature dependence of the intensity of chemiluminescence [Eq. (2)].

With the exception of the recombination of radicals, there are no elementary acts in the thermal decomposition which would give rise to quanta of sufficient energy. True, the total quantum yield of chemiluminescence η_{cl} is very low—not greater than 10^{-8}—10^{10}—and, naturally, the following question arises: Is the luminescence associated with some secondary process, whose rate w' is very much slower than the rate of the main reaction, but which has a high yield η'_{cl}, so that the product $\eta'_{cl} w'$ is not too small? The good correlation between the experimental and theoretical dependence and the possibility of obtaining the correct activation energy indicate that the answer to this question should be in the negative.

At the same time, we may expect that, in some cases, secondary processes of the aforementioned type may complicate the effect. Thus, in the case of organic hydroperoxides,[85] which are difficult to decompose, clear quantitative relationships could not be obtained.

The decomposition of peroxides is accelerated by catalysts—salts of metals of variable valence (copper, zinc, cobalt). The intensity in these cases is relatively high, because the rate of the radical recombination is high.[42-44] If catalysts are metallic compounds of complex dyes—porphyrins and chlorophyll, then the chemiluminescence spectra are identical with the fluorescence spectra of the dyes.[113,116,117]

The thermal decomposition of hydrogen peroxide in water is also accompanied by chemiluminescence, whose intensity is proportional to the rate of decomposition.[53] In contrast to the case referred to earlier, this reaction has an ionic mechanism; the excitation obviously takes place in the act of decomposition of a complex formed of the molecule H_2O_2 and the ion radical HO_2^-.

## 5. Oxidation with Molecular Oxygen in Organic Solvents

The brightness of chemiluminescence during the oxidation of hydrocarbons and their derivatives is at least an order of magnitude higher than in the thermal decomposition.

The liquid oxidation of hydrocarbons RH and of their derivatives follows a chain mechanism. At moderate temperatures only does the initial stage take place—
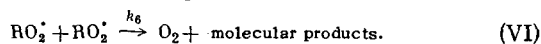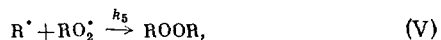
the formation of a hydroperoxide ROOH as a consequence of the following elementary acts:*

1) Nucleation (initiation) of chains—the appearance of radicals R• and $RO_2^•$ at a rate w_i.   (I)

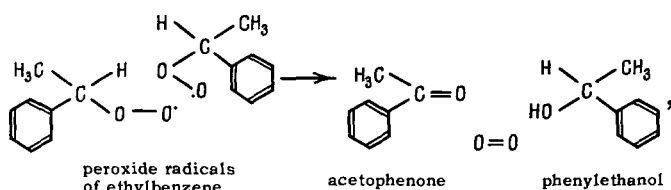2) Chain oxidation:

$$R^• + O_2 \xrightarrow{k_2} RO_2^•, \tag{II}$$

$$RO_2^• + RH \xrightarrow{k_3} ROOH + R^•. \tag{III}$$
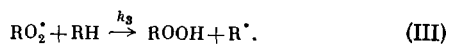
3) Breaking of chains (recombination of radicals):

$$R^• + R^• \xrightarrow{k_4} R_2, \tag{IV}$$

$$R^• + RO_2^• \xrightarrow{k_5} ROOR, \tag{V}$$

$$RO_2^• + RO_2^• \xrightarrow{k_6} O_2 + \text{ molecular products.} \tag{VI}$$

As in the thermal decomposition case, only the reactions (IV), (V), and (VI) are sufficiently exothermal. Moreover, in the presence of excess oxygen, the concentration of peroxide radicals $RO_2^•$ is found to be much higher than the concentration of hydrocarbon radicals R•, and practically the only recombination reaction is (VI), in which an unstable complex is formed which decomposes into O_2 and molecular products,[131] for example—in the oxidation of ethylbenzene:

peroxide radicals of ethylbenzene   acetophenone   phenylethanol

and in the oxidation of methyl ethyl ketone:

peroxide radicals of methyl ethyl ketone

diacetyl
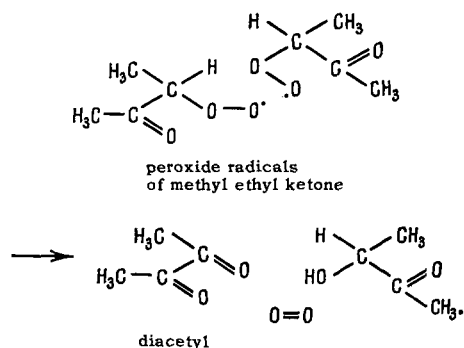
The recombination of peroxide radicals does not require an activation energy and the thermal yield, estimated as the difference of the energies of the formed and broken bonds, amounts to not less than 100 kcal/mole, which is sufficient for the excitation of luminescence in the visible region.

Under steady-state conditions, the rate of recombination is equal to the rate of initiation. If the initiation takes place due to a specially introduced ini-

*For the mechanism of oxidation in liquids, see, for example, monograph [4].

tiator (Y), the intensity of luminescence should depend on temperature and the concentration of Y, in the same way as in the thermal decomposition reactions. This is found experimentally[10,56] and it confirms the recombination nature of the excitation.

The recombination of peroxide radicals is responsible also for the chemiluminescence which appears during and after the irradiation of organic compounds with penetrating radiation.[106]

Figure 5 shows the chemiluminescence spectra obtained in the oxidation of several substances.[24] The spectrum of methyl ethyl ketone is characteristic: it repeats the structure of the photoluminescence spectrum of diacetyl (Fig. 5, curve 4'). The latter spectrum represents the superposition of fluorescence and phosphorescence, the latter being the dominant radiative deactivation[82,133] (transitions from the triplet state; Fig. 6).

The chemiluminescence spectra of other hydrocarbons are in the form of wide structure-free bands with flat maxima at 420—450 mμ. If we assume that ketones are excited in these cases, the result is not unexpected: A. N. Terenin[65,67] has shown that monocarbonyl derivatives of hydrocarbons exhibit a blue-violet luminescence, representing triplet-singlet transitions. However, since the band profiles lack individuality, the identification by spectra alone is not reliable. "In solutions," wrote S. I. Vavilov, "the spectra are very uncharacteristic, broad, and do not have fine details. Therefore, sufficiently reliable conclusions cannot be derived, in the normal sense of the word, only from the

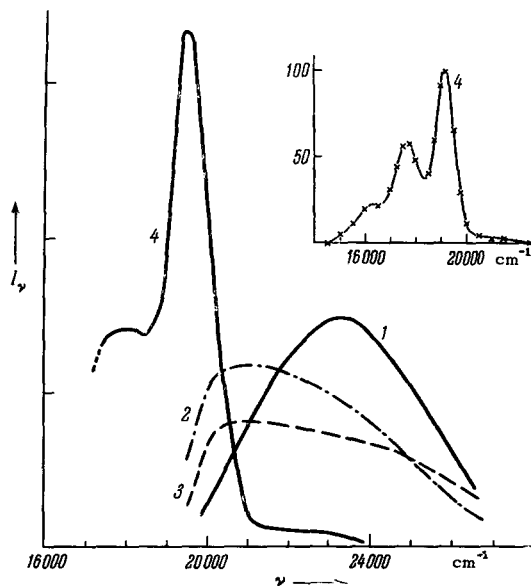FIG. 5. Luminescence spectra of ketones excited in the oxidation of ethylbenzene (1), cyclohexane (2), n-decane (3), and methyl ethyl ketone (4) at 60-65°C. [24] The entry slit was 7 mm wide and the exit slit 2 mm for a dispersion of 20 Å/mm. 4') Photoluminescence spectrum of diacetyl (according to the data in[76]). The ordinate gives the quantum spectral intensity on the frequency scale (in arbitrary units for each experiment).
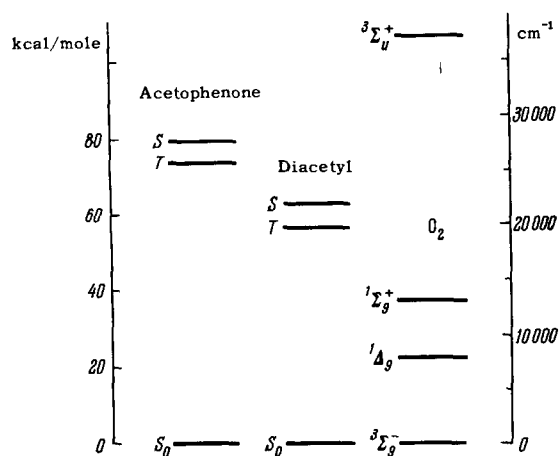
FIG. 6. Schematic diagram showing lower electron levels of acetophenone,[19] diacetyl,[62] and molecular oxygen.[33]

spectra. The understanding of the photoluminescence of solutions is greatly helped by the use of other optical properties of luminescence: intensity, polarization, and duration."[5a]

The direct determination of the excited-state lifetime (e.s.l.) τ_P and of the quantum yield of luminescence η_P is impossible in the case of chemiluminescence because, on the one hand, the excitation cannot be stopped suddenly and, on the other, the total yield of luminescence η_{cl} depends not only on the value of η_P but also on the excitation yield η_P^{exc} [cf. Eq. (1)]. However, indirect methods may be used.

The e.s.l. can be found from quenching by oxygen. Oxygen has a dual effect on chemiluminescence.[8] At low concentrations, it enhances luminescence, since it favors the transformation of hydrocarbon radicals into peroxide radicals [reaction (II)], which, recombining, give more light. [RO$_2$] depends approximately on [O$_2$] in accordance with the law [20]

$$[RO_2^{\cdot}]=\sqrt{\frac{w_i}{k_6}}\,\frac{[O_2]}{[O_2]+S},$$ (6)

where

$$S=\frac{k_3}{k_2}\sqrt{\frac{k_4}{k_6}}\,[RH]+\frac{\sqrt{k_4 w_i}}{k_2}.$$

If excited molecules are formed in the recombination of peroxide radicals, the intensity of chemiluminescence is proportional to the rate of this process and [cf. Eqs. (1) and (6)] is governed by the following expression

$$I=\eta_P\eta_P^{exc}\,k_6\,[RO_2]^2=\eta_P\eta_P^{exc}\,\omega_i\,\frac{[O_2]^2}{([O_2]+S)^2}.$$ (7)

Reaction (II) is rapid (k_2 is large) and, even in the presence of 10^{-6}—10^{-5} mole/liter of oxygen, practically all the hydrocarbon radicals appearing in the system are transformed into peroxide radicals (i.e., [O$_2$] $\gg$ S) and only the latter radicals recombine. Therefore, a further increase of [O$_2$] should not alter the intensity of luminescence. However, experiments show that, as

a rule, high concentrations of oxygen quench chemiluminescence. This effect is particularly clear if a solution is saturated with oxygen and the reaction chamber is hermetically sealed. The gradual consumption of oxygen slows down the quenching action and increases the intensity (Fig. 7a). The strong quenching at the end of the process ("oxygen drop") indicates the moment of complete disappearance of oxygen from the solution. Oxygen is consumed at a constant rate [11,21]

$$w_{O_2}=-\frac{d\,[O_2]}{dt}=\frac{k_3}{\sqrt{k_6}}\,[RH]\,\sqrt{w_i}+\frac{1}{2}\,w_i.$$ (8)

Thus, the time dependence of the process represents, at the same time, the dependence of the concentration of oxygen, and makes it possible to investigate quantitatively the influence of oxygen. The dependence of the intensity on [O$_2$] obeys the Stern-Volmer equation (Fig. 7b):

$$\frac{I_0}{I}=1+k\tau_P\,[O_2],$$ (9)

where τ_P is the excited-state lifetime of the emitter P*, and k is the quenching reaction rate constant:

$$P^*+O_2 \xrightarrow{k} P+O_2.$$
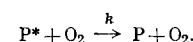
The e.s.l. is governed by all the processes of the deactivation of P*:

$$\tau_P=\left(f_P+d_P+\sum k_{Q_i}\,[Q_i]\right)^{-1},$$ (10)

where f_P and d_P are the probabilities of intromolecular radiative and radiationless transitions; k_{Q_i} are the quenching constants for other quenching substances, Q_i, present in the solution. After corrections, the experimental value of $k\tau_P$, obtained from the Stern-Volmer equation, is found to be 2×10^3 liter/mole (in the oxidation of ethylbenzene). Assuming that k has the diffusion value of 10^9—10^{10} liter·mole^{-1}sec^{-1} it is found that $\tau_P = 10^{-7}$—10^{-6} sec, which is close to the e.s.l. of the triplet acetophenone (3.6×10^{-7} sec) ob-
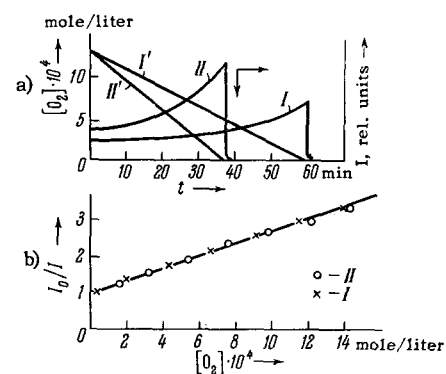

FIG. 7. Kinetic curves of the intensity (I, II) and the concentration of dissolved oxygen (I', II') in the oxidation of ethylbenzene in benzene for two experiments differing in their reaction rate. b) Curves I and II replotted in the coordinates of the Stern-Volmer equation.
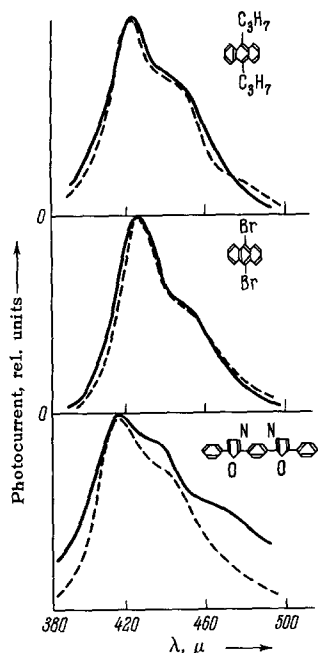
FIG. 8. Chemiluminscence spectra due to the oxidation of cyclohexane activated by phosphors (continuous curves), and photoluminescence (fluorescence) spectra of phosphors recorded using the same apparatus (dashed curves).

tained, under practically the same conditions, in the photoluminescence.[157]

Particularly strong oxygen quenching is observed in the chemiluminescence of methyl ethyl ketone.[15,24] This is in agreement with the long e.s.l. of this substance—up to 10^{-3} sec in well-purified solvents.[82]

The quantum yield of the luminescence of an excited particle can be determined from the activated chemiluminescence. The introduction of activators (A) into a solution gives rise to the energy transfer:[15,16,19]

$$P* + A \xrightarrow{k_{PA}} P + A*.$$
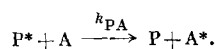
The energy transfer is followed by the emission from the activator:

$$A* \xrightarrow{f_A} A + h\nu_A.$$
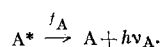
Naturally, in this case, the spectrum, yield, and e.s.l. represent the activator molecule and not the particle excited first. For example, the addition of derivatives of anthracene and oxazole makes the luminescence spectrum identical with the fluorescence spectrum of the activators (Fig. 8) and the e.s.l. is shortened so much that the oxygen quenching of chemiluminescence practically disappears[21] (τ_A is of the order of 10^{-8} sec[70]).

As a rule, activators enhance chemiluminescence.[15] It follows from Fig. 9 that the enhancing effect of activators increases with their concentration in accordance with the law obtained in[16]:

$$\frac{1}{\varkappa - 1} = \frac{\eta_P}{\eta_A - \eta_P} + \frac{1}{\eta_A - \eta_P} \frac{f_P}{k_{PA}} \frac{1}{[A]}, \qquad (11)$$
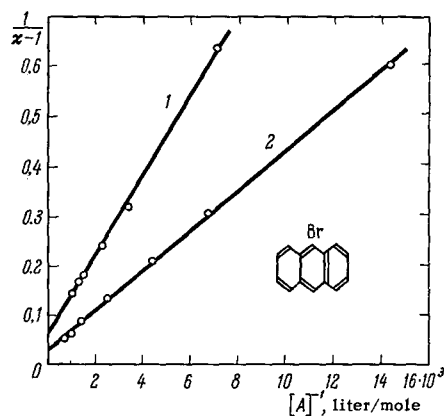

FIG. 9. Dependence of the gain of the luminescence on the concentration of 9-bromanthracene in the oxidation of ethylbenzene in benzene, plotted in coordinates of Eq. (11). Initiators: 1) azobisisobutyronitrile (1.22×10^{-2} mole/liter) at $50.0°$C; 2) dicyclohexylperoxydicarbonate (4.3×10^{-3} mole/liter) at $30.0°$C.
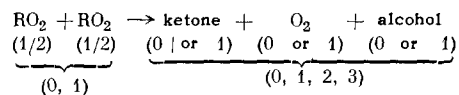
where $\varkappa$ is the enhancement coefficient or the ratio of the intensity in the presence of an activator to the intensity in the absence of an activator. Using Eq. (11), the quantum yield of the luminescence of an emitter can be found from the known fluorescence yield of the activator η_A for the oxidation of ethylbenzene and cyclohexane: $\eta_P = 5 \times 10^{-4} \pm 60\%$.[25]

The quantum yield and the e.s.l. are measured independently. Their ratio should be equal to the probability of a radiative transition in the product molecule:

$$\frac{\eta_P}{\tau_P} = f_P.$$

An estimate gives a value of the order of 10^3 sec^{-1},[21] which is typical of the triplet-singlet radiative transitions.[39,40]

A comparison of the quantitative characteristics of an excited particle with the spectra and chemical mechanism of the reaction shows that the emitters of chemiluminescence in the oxidation of hydrocarbons are carbonyl compounds in excited electronic (mainly triplet) states.[21,24,25]* In the recombination of radicals, Wigner's rule does not impose restrictions on the multiplet state of the products formed, as can be easily seen from the reaction equation

$$
\begin{array}{ccccc}
RO_2 & + RO_2 & \rightarrow \text{ketone} + & O_2 & + \text{ alcohol} \\
(1/2) & (1/2) & (0 \text{ or } 1) & (0 \text{ or } 1) & (0 \text{ or } 1) \\
\underbrace{\qquad}_{(0, 1)} & & \underbrace{\qquad\qquad}_{(0, 1, 2, 3)} & &
\end{array}
$$

(the numbers in parentheses give the spin values).

---

*In,[27] the luminescence in the region of 430–450 mμ, observed during the oxidation of hydrocarbons, has been ascribed to the excited oxygen molecule, formed in reaction (VI). This interpretation causes confusion, because the population of the $^3\Sigma_u^+$ state (106 kcal/mole; cf. Fig. 6), which can give rise to radiation in the visible region, is doubtful even in the case of recombination of O atoms[89] and is hardly possible under the relatively "soft" conditions of reaction (VI).

Table I. Mechanism of chemiluminescence during the oxidation of hydrocarbons (RH) in solution

Process	Equation
Recombination of peroxide radicals producing unexcited ketone	$2RO_2^{\bullet} \xrightarrow{k_6} O_2 + alcohol + ketone(P)$
Ditto, producing ketone in the triplet state	$2RO_2^{\bullet} \xrightarrow{\eta_P^{BO36}k_6} O_2 + alcohol + P^*$
Chemiluminscence	$P^* \xrightarrow{f_P} P + h\nu_P$
Internal deactivation of P*	$P^* \xrightarrow{d_P} P$
Deactivation of P* by quenching substances Q_i	$P^* + Q_i \xrightarrow{k_{Q_i}} P + Q_i$
Transfer of excitation energy to activator A	$P^* + A \xrightarrow{k_{PA}} P + A^*$
Luminescence of activator (activated chemiluminescence)	$A^* \xrightarrow{f_A} A + h\nu_A$
Deactivation of A*	$A^* \xrightarrow{d_A} A$
	$A^* + Q_i \xrightarrow{k'_{Q_i}} A + Q_i$

Therefore, the products can be obtained both in the triplet as well as in the singlet states. The fact that, in the oxidation of ethylbenzene, the emitter is the triplet acetophenone is solely due to the rapid conversion from the singlet to the triplet state, which is characteristic of this substance, [39] and the reaction obviously populates both states. In the oxidation of methyl ethyl ketone, there are transitions both from the triplet and from the singlet states (cf. Fig. 5).

The heat of recombination of peroxide radicals is sufficient also for the excitation of the levels $^1\Sigma_g^+$ and $^1\Delta_g$ of the molecular oxygen (cf. Fig. 6); its luminescence lies in the infrared part of the spectrum (as established by means of light filters) [26]

The mechanism of chemiluminescence in the visible region can be represented by the scheme given in Table I (the symbols above the arrows represent the rate constants of the processes).

The following expression is obtained from this scheme for the quantum intensity of chemiluminescence

$$I = f_P [P^*] + f_A [A^*] = \{\eta_P (1 - \eta_{PA}) + \eta_A \eta_{PA}\} \eta_P^{exc} w_{rec}, \qquad (12)$$

where

$$w_{rec} = k_6 [RO_2]^2$$

is the rate of recombination of radicals;

$$\eta_P = f_P (f_P + d_P + \sum_i k_{Q_i} [Q_i])^{-1}$$

is the quantum yield of luminescence for P*;

$$P^*; \eta_A = f_A (f_A + d_A + \sum k'_{Q_i} [Q_i])^{-1}$$

is the quantum yield of luminescence for A*;

$$A^*; \eta_{PA} = k_{PA} [A] (f_P + d_P + \sum k_{Q_i} [Q_i] + k_{PA} [A])^{-1}$$

is the probability of energy transfer.

According to Eq. (12), the intensity of luminescence is proportional to the reaction rate. However, the coefficient of proportionality depends on the concentrations of the quenching substances and activators. The quenching substances may be, in particular, some inhibitors, solvents, as well as some reaction products, impurities, and the oxidized hydrocarbons themselves. [15,25] Therefore, frequently the intensity of chemiluminescence does not increase in proportion to the concentration of inhibitors [as would be required by Eqs. (3)—(5)], but more slowly (Fig. 10).

Equation (12) allows us to describe quantitatively the effect of an initiator Y which has a quenching effect; from this equation, we can easily obtain:

$$\frac{[Y]}{I} = \left(\frac{[Y]}{I}\right)_0 (1 + k_Y \tau_P [Y]),$$

where k_Y is the rate constant for the deactivation by the initiator. The dependence is satisfied well experi-
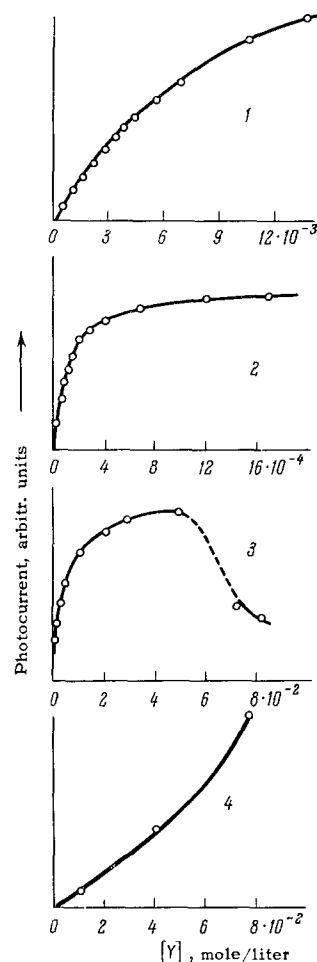

FIG. 10. Dependence of the intensity of chemiluminescence in oxidation reactions on the concentration of initiators: dibenzoylperoxide in ethylbenzene (1); azobisisobutyronitrile in a mixture of ethylbenzene + acetic acid (2) and in ethylbenzene (3); dicyclohexylperoxydicarbonate in a mixture of ethylbenzene + benzene (4).
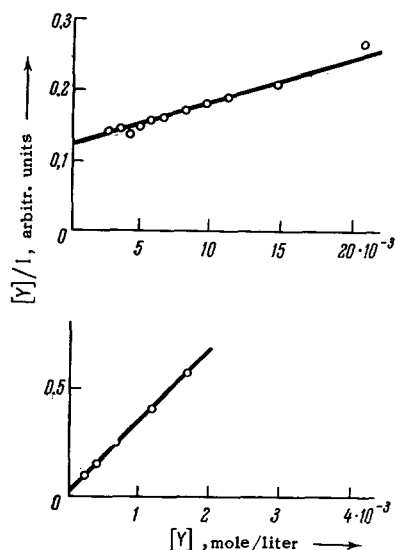
FIG. 11. Dependence of the ratio of the concentration of an initiator and the intensity of luminescence on the concentration of initiators for experiments 1 and 2 in Fig. 10.

mentally (Fig. 11). The values of $k_Y \tau_p$ are found to be of the order of 10^3 liter/mole, which, on the assumption of the diffusion nature of quenching ($k_Y \approx 10^{10}$ liter·mole^{-1}sec^{-1}), leads to values of the e.s.l. that agree with those estimated from oxygen quenching (of the order of 10^{-7} sec).

The energy transfer of luminescing components ("intrinsic" activators) plays a smaller role and is not observed frequently. In the initiation with dicyclohexylperoxydicarbonate, the rise in the intensity is faster than the increase in concentration (Fig. 11); it is possible that the initiator, which has C=O groups, is a weak activator. [21] The increase in intensity with time in the decomposition of ditertbutylperoxide in chlorobenzene [73] is due to the accumulation of strongly luminescing products.

Thus, secondary processes may greatly complicate the effect, and this should be always borne in mind.*

When the characteristics of chemiluminescence (the spectrum, yield, e.s.l.) represent the particle which was excited first, the energy transfer can be ignored and Eq. (12) assumes the simple form of Eq. (1). The simultaneous measurements of the absolute intensity and of the reaction rate makes it possible to determine the total quantum yield of chemiluminescence: $\eta_{cl} = I/w = \eta_p \eta_p^{exc}$. This quantity is small (of the order of 10^{-10} for the oxidation of cyclohexane and n-decane; 10^{-9} for ethylbenzene; 10^{-7} for methyl ethyl ketone [24]) and is mainly governed by the low excitation yield. The low value of η_p^{exc} is most probably

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*The transfer of energy to specially introduced activators has also been observed in strongly luminescent reactions.[59,109,121,150]. The possibility of the influence of "intrinsic" activators on the chemiluminescence in liquid-phase reactions has not been considered before. The mechanism of the energy transfer has not been investigated at all.
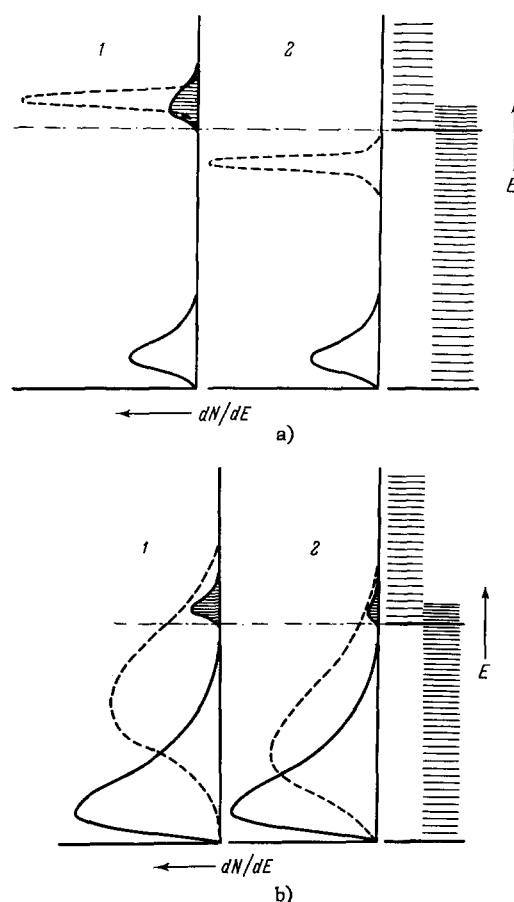

FIG. 12 Distribution of the electronic and vibrational levels of the products from the recombination of radicals (qualitative representation). Dashed curves represent the situation immediately after a reaction. Continuous curves represent thermal equilibrium with a medium. The shaded areas are proportional to the number of electron-excited molecules. Cases 1 and 2 represent, respectively, stronger and weaker thermal effects of the reaction, other conditions being equal. In case a), only one product is formed, and the initial distribution is more peaked than in case b), which corresponds to the formation of more than one product.

due to the fact that, in most cases, the energy, accumulated molecules, is insufficient for the excitation.

Figure 12 show qualitatively the distribution of the product molecules according to their vibrational levels both immediately after a reaction and after a time interval which is sufficient to establish equilibrium with the medium but shorter than the lifetime of the excited electron state. The distribution function has a maximum: as the energy increases, the population of the vibrational levels decreases but their density increases because of the anharmonicity. For clarity, only one system of vibrational levels is shown in Fig. 12.

If a reaction gives rise to one product (for example, the recombination of hydrocarbon radicals), then in each act the whole liberated energy is concentrated in one molecule [case a)]. The initial distribution is

peaked and reflects only the Maxwell-Boltzmann distribution of the initial reagents (radicals). The probability of excitation may be high if the exothermal energy of the reaction is greater than the excitation energy; it is equal to zero if the reverse is true. If the recombination gives rise to several products (recombination of peroxide radicals), the distribution is broader [case b)]. Although this discussion is of a qualitative nature, it follows clearly that one should not expect the dense population of a level lying at 70—75 kcal/mole for a heat of recombination of 100—120 kcal/mole, shared between three molecules (alcohol, ketone, and oxygen).

Another reason for the low yield may be the quenching by O_2 molecules, which are (immediately after the reaction) in the immediate vicinity of the excited product and which may deactivate this product.

For ethylbenzene and cyclohexane, $\eta_P^{exc} = 10^{-6}-10^{-5}$; the corresponding steady-state concentration of excited molecules is low—of the order of 10 molecules/cm^3.[24]

The excitation quantum yield has the meaning of the probability of formation of one of the products of an elementary exothermal act in a definite energy state. This characteristic is of great interest in the theory of chemical reactions, for the understanding of the processes controlling the distribution and redistribution of energy between products. Such problems are being intensively investigated in the case of reactions of simple molecules in the gaseous phase.[124,127,128] Similar investigations have not yet been carried out for reactions in solutions. We may assume that systematic measurements of the excitation yields of products in liquid-phase reactions (ketones; oxygen in the oxidation of monotypic compounds) will produce much information of value in the theory of elementary reactions in solutions.

6. Oxidation in Aqueous Solutions

Recently, Stauff and his colleagues[142-145] investigated the weak chemiluminescence accompanying the oxidation of many substances: N_2H_4, H_2SO_4, $NaHSO_3$, $K_3Fe(CN)_6$, urea, gelatine, etc. The oxidizing agents were: hydrogen peroxide, molecular oxygen (as a rule, together with a catalyst), sodium hypochlorite NaClO, and sodium hypobromite NaBrO.
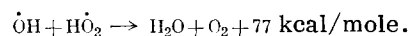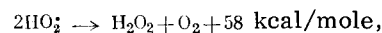
In the catalytic oxidation of aqueous solutions of $NaHSO_3$ with molecular O_2, the luminescence maximum was at 480 mμ. The kinetic intensity curve had two peaks. In the opinion of Stauff et al., one peak is due to the transfer of an electron in a complex formed with the catalyst and to the formation of the ion O_2^-; the second peak is due to the recombination of HO_2^* radicals. According to Stauff et al., the confirmation of this explanation was provided by the fact that inhibitors, which captured free radicals, quenched chemiluminescence.[144,145]

The spectra of the reactions of oxidation of hypohalide compounds had maxima at 580 and 530 mμ,

which were not very characteristic, and, in the neutralization reactions, maxima were at 480 mμ. In the majority of the reactions, the intensity of the luminescence first rapidly increased and then decreased slowly in accordance with the law

$$I^{-1/2} = I_0^{-1/2} + at, \tag{13}$$

where the coefficient α was inversely proportional to $[O_2]$. Stauff was of the opinion that the excited particle was a complex of two O_2 molecules bound by van der Waals forces. The complex was formed when two electron-excited O_2 molecules met. This happened on the recombination of the radicals HO_2^* and $\cdot OH$, whose presence was detected by the EPR method:[146]

$$2HO_2^* \rightarrow H_2O_2 + O_2 + 58 \text{ kcal/mole,}$$

$$\dot{O}H + H\dot{O}_2 \rightarrow H_2O + O_2 + 77 \text{ kcal/mole.}$$

The energy evolved in these reactions was sufficient to excite the states $^1\Delta_g$ and $^1\Sigma_g^+$ (cf. Fig. 6). The maxima in the chemiluminescence spectra could be ascribed to the transitions: $^1\Sigma\,^1\Delta \rightarrow\,^3\Sigma\,^3\Sigma$ (480 mμ), $^1\Delta\,^1\Delta + \omega \rightarrow\,^3\Sigma\,^3\Sigma$ (580 mμ), $^1\Delta\,^1\Delta + 2\omega \rightarrow\,^3\Sigma\,^3\Sigma$ (530 mμ), where ω was a vibrational quantum for O_2; these maxima were close to the absorption maxima of the $(O_2)_2$ complexes. Some kinetic schemes of the formation of $(O_2)_2^*$ led to a theoretical dependence of the type given by Eq. (13) and to an experimentally observed proportionality between I and $[O_2]^2$.

In the reactions of the hypochlorite NaClO and of Cl_2 with H_2O_2 in water, Seliger[135] found in 1960 a band at 635 mμ, and, later,[136] two more bands: 703 mμ and (very weak) 578 mμ. Since the difference between the wave numbers, 1570 cm^{-1}, was close to the frequency of vibrations in the O_2 molecule (1580 cm^{-1}), this band was ascribed[111] to the vibrational components (0, 0) and (0, 1) of the transition $^1\Sigma_g^+ \rightarrow\,^3\Sigma_g^-$ (cf. Fig. 6), and a short-wavelength shift by 2600 cm^{-1}, with respect to the transition in gaseous O_2, was ascribed to the influence of the solvent. Although the possibility of such a large shift had been demonstrated by a theoretical calculation,[101] this interpretation was found to be premature because the same bands were found in the gaseous phase (in an electrical discharge in O_2).[78] Later, Browne and Ogryzlo[90] ascribed the chemiluminescence spectrum over a wide region to the reaction $Cl_2 + H_2O_2$ (Fig. 13) and gave the following interpretation: 12,700 and 10,700 Å—the components (0, 0) and (0, 1) of the transition $^1\Delta_g \rightarrow\,^3\Sigma_g^-$; 7619, 8645, and 7700 Å—the components (0, 0), (0, 1), and (1, 1) of the transition $^1\Sigma_g^+ \rightarrow\,^3\Sigma_g^-$. The three peaks in the orange-red region were ascribed to the components (1, 0), (0, 0), and (0, 1) of the electron transition $^1\Delta_g\,^1\Delta_g \rightarrow\,^3\Sigma_g^-\,^3\Sigma_g^-$ in the $(O_2)_2$ complex.

The chemiluminescence spectra of many oxidation reactions in gaseous solutions are very similar;[147] this is because the radicals $\dot{O}H$ and $H\dot{O}_2$ take part in
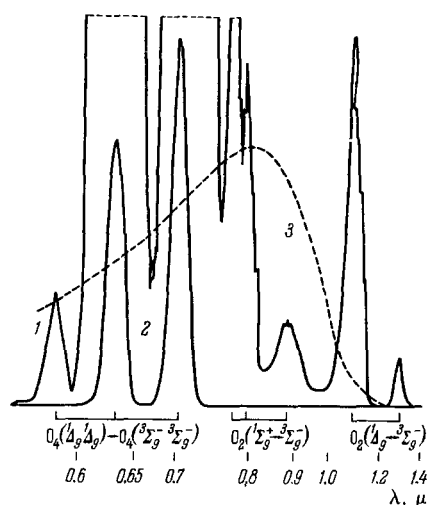
FIG. 13. Chemiluminescence spectrum for the reaction of chlorine with hydrogen peroxide in an alkaline aqueous solution.[90] The scale of curve 1 is 1000 times greater than that of curve 2; 3) relative spectral sensitivity of the photomultiplier.

these processes and the reactions of these two radicals can produce excited oxygen and its dimer $(O_2)_2^*$.

It should be noted that the concentration of the complex $(O_2)_2^*$ should be very low because, first two excited molecules must meet to form it; and, secondly, the lifetime of this complex is very short (for the unexcited complex it amounts to only 10^{-13} sec [38]). It follows that side reactions may compete successfully with the excitation and luminescence of the complex $(O_2)_2$. For these two reasons, the luminescence should be very weak—which is indeed observed experimentally.

## III. OTHER FORMS OF CHEMILUMINESCENCE

7. Bioluminescence

Complex chemical (biochemical) processes in living organisms are sometimes accompanied by luminescence.

Many types of animal and plant are capable of luminescing: bacteria, fungi, radiolaria, sponges, corals, hydras, sea worms, crustaceans, mollusks, snails, centipedes, insects, sea fishes. With certain exceptions, luminescence is not exhibited by the higher forms of plants, amphibians, reptiles, birds, and mammals; fresh-water organisms do not luminesce, even if they are closely related to luminescent types of organisms living in seawater.

Investigations of the bioluminescence of various living organisms led to the conclusion, fifty years ago, that the luminescence is due to the oxidation, with oxygen, of a substance called luciferin, and the reaction is catalyzed by an enzyme called luciferase. Both luciferins and luciferases are specific for given luminescent organisms. The structure of these compounds has not been determined until very recently. Not long ago,[120,137,139] it became possible to separate pure

luciferin and luciferase from the glands of the Photinus pyralis fly, as well as to identify and synthesize chemically luciferin, which has the following structure:
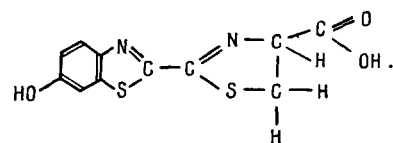

In the luminescence stage luciferin is oxidized with molecular oxygen, forming oxyluciferin and water:
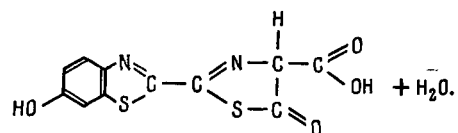
Luciferase is a protein molecule which includes more than 1000 aminoacid units. The component essential to luminescence is adenosinetriphosphate. The dependence of the luminescence intensity on the concentration of adenosinetriphosphate is the basis of the method by means of which we can measure very small amounts (10^{-10}—10^{-9} g/ml [69]) of this substance, which is the universal provider of energy in biochemical processes taking place in living organisms.

A surprising result was obtained in the measurement of the quantum yield of this reaction. It was found that, on the average, 0.88 photons are obtained per one oxidized molecule of luciferin.[137] Such a high quantum yield has not yet been observed in any chemiluminescent reaction. Obviously, the excited particle is the oxidized luciferin molecule. Before oxidation, it forms a complex with the enzyme and with adenosinetriphosphate; the complex reduces the probability of deactivation in collisions with neighboring molecules.

Luciferin in the crustacean Cypridina has the following structure:[105,140]
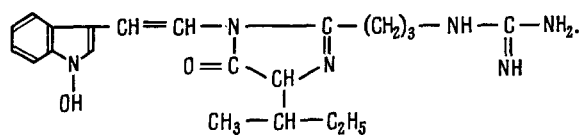
In the opinion of McElroy and Seliger,[120] the ability to luminesce is a rudimentary attribute which has developed during the evolution of life on Earth.[120] It is possible that the first organisms to appear on Earth were capable of existing in the absence of oxygen. When oxygen began to appear in the atmosphere, it had an unfavorable etching effect on these organisms. By natural selection, only those forms of life survived which developed an ability effectively to "destroy" the molecular oxygen reaching them by, say, converting it into water. The energy evolved in this way could excite molecules and give rise to luminescence.

In the early 1920's, A. G. Gurvich and his colleagues[36,37] reported that some plant and animal tissues emitted very weak radiation in the 190—325 mμ

region. They were able to show that the radiation was due to mitosis, i.e., cell division. Moreover, it was found that this radiation enhanced mitosis in some tissue cultures.* On this basis, very sensitive biological radiation detectors were developed, which were used to investigate the radiation called mitogenetic radiation. Later, this radiation was also recorded by means of physical detectors but the signals were almost always of the same order as the noise.

Weak visible radiation was recently recorded in many biological systems, including living tissues and organs.[31,41] †

Investigations of the weak chemiluminescence of systems capable of photochemical reactions (in particular, photosynthesis[29]) are of great importance in the determination of the mechanism of photosensitive and enzyme reactions, and of the storage and migration of energy.

8. Heterogeneous Oxyluminescence

In 1945, A. N. Terenin and L. A. Kachur[66] observed a visible luminescence of heated magnesium oxide powder when air, saturated with organic vapors of the following substances, was passed over it:

C_2H_5OH, CH_3CHO, CH_3COOH, $(CH_3)_2CO$, $C_6H_5CH_3$, $C_6H_5CH_2OH$.
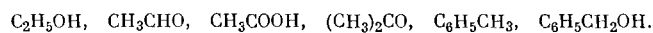
They showed that the luminescence was a chemiluminescence caused by the oxidation of organic substances on the surface of magnesium oxide, the latter acting as a catalyst. The emitters were highly condensed products of oxidation or a range of such products; they were probably excited by the transfer of energy from the primary oxidation products.

9. Candoluminescence

In 1925, Bonhöffer[84] showed that crystal phosphors luminesced under the action of atomic hydrogen. Later, similar luminescence was observed under the action of other free atoms and radicals—in particular, those formed in flames. The phenomenon—called candoluminescence—is caused by the recombination, on the surface of a phosphor, of free atoms and radicals.[34,132]

It should be mentioned that for a long time there was no agreed view on the nature and mechanism of candoluminescence. Some authors ascribed the phenomenon to oxidation-reduction processes; others rejected altogether the superequilibrium nature of the luminescence and explained the experimental observations in terms of the features of pure thermal radiation of bodies under flame conditions. Only recently, V. A. Sokolov and his colleagues[30,34] obtained clear

experimental proof of the recombination mechanism of the phenomenon.

Very recently, allowance has been made for the fact that a crystal phosphor can be a semiconductor as well as a recombination catalyst. The characteristics of the phenomenon have been considered on the basis of the electron theory of chemisorption and catalysis, and the theoretical consequences have been confirmed qualitatively by experiments.[30]

10. Luminescence during the Recombination of "Frozen" Radicals

Methods have recently been found for producing high concentrations of active free radicals. For this purpose, either the products of electrical discharges or photolysis were deposited on a cold surface, or frozen solutions and solids were photolyzed or radiolyzed. On thawing or dissolving, the radicals reacted with one another. Luminescence was then frequently observed.

Flashes of yellow-green light appeared on thawing γ-irradiated solutions of aromatic compounds,[94] and green-blue flashes were seen on heating products of the interaction of H atoms with HN_3 or N_2H_4.[125] The formation of excited ethylbenzene was observed on thawing the products of photolysis of diazomethane CH_2N_2.[99]

Weak chemiluminescence was also observed during the dissolving of irradiated desoxyribonucleic acid,[75] protein,[61,148] and polymethylmethacrylate.[61]

The chemiluminescence observed when "frozen" radicals recombine should be distinguished from other types of luminescence, which are observed when irradiated samples are heated—for example, the recombination of electrons with holes.[54]

11. Luminescence during Electrolysis

In electrochemical reactions, primary oxidation and reduction products are, as a rule, unstable and extremely reactive. Therefore, the amounts of energy evolved in reactions between the active products of electrolysis may be sufficient to excite visible chemiluminescence. In fact, weak luminescence has been observed in the electrolysis of ethanol, acetic acid, potassium acetate,[10,73] carboxylic acid salts, many organic substances, and Grignard reagents.[76]

Schlyapintokh et al.[74] carried out electrolysis, using platinum electrodes, of a 0.1 N solution of NaOH, to which they had added 5×10^{-5} mole/liter fluorescein or eosin. At room temperature, using a voltage of 10—30 V and a constant current of several milliamperes, an intense chemiluminescence was observed at the anode. Electrolysis caused by alternating currents of various frequencies made it possible to detect additional chemiluminescent processes and to estimate the lifetime of the active anodic products (this lifetime was of the order of 1 sec).

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*Recently, S. V. Konev[51] reported the acceleration of cell division in yeast under the action of weak fluxes (10^5 photons.cm^{-2} sec^{-1}) of ultraviolet light from a mercury lamp.

† See collection: Biolyuminestsentsiya (Bioluminescence) (Symposium held June 3–6, 1963), Nauka, Moscow, 1965.

12. Sonoluminescence

It is known that cavitation (loss of continuity) of some liquids under the action of ultrasound is accompanied by weak luminescence. The mechanism of this luminescence (known as sonoluminescence) has not yet been finally established. In addition to theories proposing thermal excitation (on compression) or electric discharges, there are also indications that this is luminescence due to reactions caused by ultrasound.[100,102]

IV. APPLICATIONS OF CHEMILUMINESCENCE

13. Analytic Applications of Reactions with Bright Luminescence

Right from the early stages of investigation of chemiluminescence in liquids, various applications of the luminescence of luminol, lucigenin, lophine, etc. have been proposed.

We have mentioned that hydrogen peroxide and a catalyst (for example, copper) are essential for the luminescence of luminol. When the concentration of any of the substances mentioned is less than a certain limit, the intensity decreases and this may be used in a quantitative analysis for this compound. Moreover, we can, also detect the compounds which react with luminol, H_2O_2, or a catalyst. In particular, the chemiluminescence method may be used to detect the presence of such compounds as hydrogen peroxide, sodium hypochlorite, copper, acetalaldehyde, glucose, vitamin C, phenol, pyrocatechol, resorcinol, pyrogallol, aniline, nitroaniline, methyl, ethyl, and propyl alcohols, etc.[57a,58] The sensitivity of the method to H_2O_2 may be extended to 10^{-7} mole/liter.[118] The sensitivity to metals is $10^{-8}-10^{-6}$, which is more sensitive than the radioactivation method.[2,3] The treatment of alkaline solutions of luminol with gases containing the groups CN and PF (nerve-paralyzing poisonous gases) causes chemiluminescence. The intensity of this luminescence depends linearly on the concentration of the gases.[98]

The chemiluminescence of luminol, enhanced by small amounts of hemin, has been suggested for use in criminology for the detection of traces of blood at the scene of a crime.[52]

The substances whose chemiluminescence depends strongly on the pH of the medium can be used successfully as indicators in quantitative analysis by titration.[52,57b]

Thus, any empirically established influence of a reagent on the intensity or the light sum of luminescence may be used as the basis of a quantitative method of analysis for a given substance, even if there is little information on the chemiluminescence mechanism. The chemiluminescence which appears on mixing luminol and alkali solutions has been used[97] as a method for solving the hydrodynamic problem of the boundary of a jet of liquid entering another liquid.

14. Determination of the Kinetic Characteristics of Oxidation Reactions

When hydrocarbons are oxidized, the excited states appear on the recombination of radicals and the chemiluminescence intensity is related in a regular way to the reaction kinetics. This has been used as the basis of chemiluminescent methods of measuring the quantitative characteristics of oxidation reactions.*

Thus, for example, the "oxygen drop" of chemiluminescence (cf. Sec. 5 and Fig. 7) can be used to measure the absolute oxidation rate, the concentration of oxygen in a liquid or gas, the relationships between the elementary constants $k_3/\sqrt{k_6}$ and $k_2/\sqrt{k_4}$, and the initiation rate.[12-14,18] Measurements of the intensity of chemiluminescence have yielded the relative[12] and absolute[46,47] values of the constants characterizing the activity of inhibitors, as well as new data on the mechanism of decomposition of azocompounds[18] and hydroperoxides.[42-44] From the temperature dependence of the intensity, we can determine rapidly the activation energy,[10,73] and from the kinetic curves, the absolute constants for the recombination of radicals.[28]

The facility for obtaining valuable quantitative information shows that chemiluminescence can be used as an effective physical method for the investigation of reaction kinetics.

The quantity measured in the experiments is the intensity of luminescence. Therefore, the chemical part of the apparatus is very simple and consists of a thermostat and a container with a thermostatted jacket. The intensity is recorded continuously and automatically by standard instruments. The high reproducibility, accuracy, and reliability of the results obtained are the benefits of these features. A high accuracy (1—2%) is achieved in those methods in which not the intensity of luminescence but the time from the beginning of the reaction to a special point on the kinetic intensity curve (for example, the "oxygen drop") is measured. The measurements do not require changes in the chemical part of the apparatus. The sensitivity of the chemiluminescent methods can be enhanced by the introduction of activators.

Chemiluminescence methods are of special importance in the investigation of the mechanism of chemiluminescence itself. In the investigation of chemiluminescence (its intensity and spectrum, and the variation with time of these), it is very important to introduce parallel control of the reaction rate (i.e., the excitation rate). This can be done conveniently by chemiluminescence methods since, in this case, there is no need to carry out separate experiments in chemical apparatus and, consequently, there is no problem of the identity of the conditions.

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*These methods are discussed in detail in the review[56]

In the radical reactions, the chemiluminescence is associated with the recombination of free radicals. It is interesting to compare the chemiluminescent methods with another physical method of recording free-radical states, i.e., with electron paramganetic resonance. We can easily see that these methods complement one another. A high rate of annihilation of radicals, i.e., their high reactivity, would favor the use of chemiluminescence methods. The EPR method can be used successfully in the case of a high steady-state concentration of radicals, i.e., when they are chemically stable. When eventually the sensitivity of these two types of method is increased, the situation becomes less of the alternative type and the simultaneous use of both methods should give interesting results. The first example of such a study is [61], in which the discovery of weak radiation during the dissolution of irradiated protein and polymethylmethacrylate was reported. The kinetics of the intensity decay was identical with the kinetics of decrease of the number of free radicals, measured in an EPR spectrometer (Fig. 14). Both methods gave important information on the protective effect of inhibitors on the irradiated system (model used to investigate radiation burn).
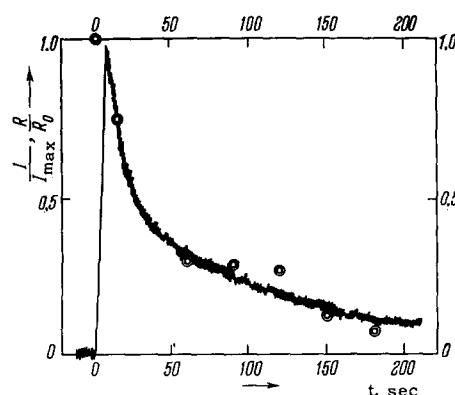

FIG. 14. Decay of the intensity of chemiluminescence (curve) and the EPR signal (points) with time from the dissolution of irradiated polymethylmethacrylate in dichloroethane.[61]

15. Investigation of Properties of Excited Molecules

The behavior of excited molecules should be independent of the excitation method. Nevertheless, each method has its own characteristics which may make it difficult to interpret the results. Therefore, it is desirable to use other excitation methods in a study of the excited states. If an excited product is identified in a given reaction, then we can speak of chemiluminescence as a method of exciting a given particle and investigating its properties.

Chemical excitation is used widely in gaseous systems.[32,33] This is the only method of obtaining spectra of physically stable but chemically unstable particles (for example, C_2, HCO, ClO, IF, etc.), because they can be accumulated in considerable amounts only under the conditions of intense chemical reactions.

This method has only recently been applied to the liquid-phase reactions. The first example of such an application, considered in [15,16,22], is the intermolecular transfer of energy from the triplet levels of ketones, formed in the oxidation of hydrocarbons, to the singlet (fluorescence) levels of activators (anthracene derivatives). The transfer itself has been proved spectroscopically (cf. Fig. 8), and the dependence of the intensity of the activated chemiluminescence on the concentration of the activator [cf. Eq. (11)] has been used to obtain the relative and absolute rate constants for energy transfer k_{PA}.

For anthracene, and alkyl- and phenyl-anthracenes, the constants k_{PA} do not exceed 10^7 liter·mole^{-1}sec^{-1}, but they increase by 1—3 orders of magnitude when heavy atoms of chlorine and bromine are introduced

into the molecules. Thus, for dibromanthracene $k_{PA} \approx 10^9$ liter·mole^{-1}sec^{-1}, which is only 1.5—2 orders of magnitude less than the number of collisions, calculated from the diffusion theory formulas.

The transfer of energy during the contact between the electron shells of molecules has been considered theoretically by Dexter[95] (see also [40]). In the overlap region, an excited electron may be transferred from a donor to an acceptor, and an unexcited electron from an acceptor to a donor. The probability of such a transfer is non-zero only if the multiplet nature of the excited states of a donor and an acceptor is the same, and if the multiplet nature of the normal states is identical. We can easily see that this selection rule is not satisfied in the case considered here, because the excited state of the donor is a triplet, and in the acceptor case it is a singlet. Therefore, the energy transfer constant k_{PA} is small (of the order of 10^7 liter·mole^{-1}sec^{-1}) in the case of anthracene and its alkyl- and phenyl-derivatives.

The introduction of halogens into an acceptor enhances the interaction between the spin and orbital magnetic moments of electrons and this gives rise to the "mixing" of the triplet and singlet states. Now, the energy transfer becomes allowed and the greater the admixture of the triplet to the singlet, the more permissible the transfer becomes. The constant k_{PA} becomes larger. For a quantitative estimate of the spin-orbital effects, it is frequently sufficient to use the approximation in which the spin-orbital coupling constants of free atoms are employed,[109] which is, in a sense, equivalent to the introduction of a rough model of a molecule, whereby it is represented as a system in which individual atoms interact independently with the excited electron. The contribution of each atom may be approximated by the quantity ζ_i^2, where ζ_i is the radial component of the matrix element of the spin-orbit interaction operator for a free atom, which is a quantity well known from atomic spectra. Within the framework of this model, we may expect the constant k_{PA} to be proportional to the sum
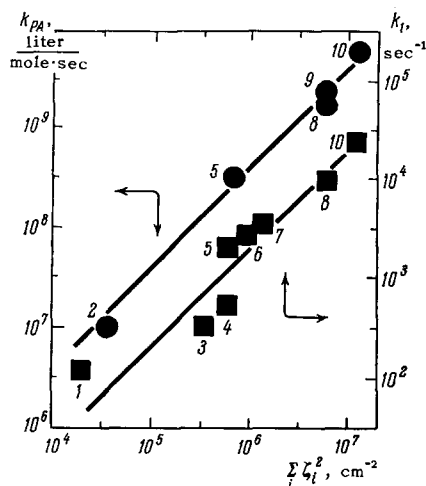
FIG. 15. Influence of substitution on the constants k_{PA} and k_t; k_{PA} taken from experiments on the oxidation of cyclohexane at 50°C in benzene,[22] k_t - from [107]. 1) Anthracene (A); 2) 9,10-diphenyl-A; 3) 1-chlor-A; 4) 1,5-dichlor-A; 5) 9,10-dichlor-A; 6) 2,9,10-trichlor-A; 7) 1,5,10-tetrachlor-A; 8) 9-brom-A; 9) 9-brom-10-phenyl-A; 10) 9,10-dibrom-A.

of the quantities ζ_i^2 for all the atoms in a molecule (the greatest contribution is then made by heavy atoms because $\zeta_C = \zeta_H = 28$ cm^{-1}, $\zeta_{Cl} = 587$ cm^{-1}, $\zeta_{Br} = 2460$ cm^{-1}). This is, in fact, observed experimentally (Fig. 15). It is worth noting that the introduction of halogens increases also the probability of the intramolecular radiation-less triplet-singlet transition k_t,[107] to the same degree to which the intermolecular transition constant is increased. This is because, simultaneously with the appearance of the triplet admixture to the singlet state, a similar admixture of the singlet type appears in the triplet state and the intercombination prohibition is weakened for both transitions.

Thus, in the case considered, the triplet-triplet transfer of energy takes place in a modified form; this effect was first observed by A. N. Terenin and V. L. Ermolaev[68] in solid solutions. In liquids, the triplet-triplet transfer has constants equal to the diffusion constants,[82,129,133] which is in agreement with the quantitative relationships governing the activated chemiluminescence.

The example given shows the promising nature of the applications of the reaction chemiluminescence with a known mechanism in the investigation of excited states.

The chemiluminescence method has the following advantages: 1) the excitation is uniform throughout the volume; 2) there is no background to the excitation source and radiation of very low yield may be recorded; 3) the actual amounts of energy are small (2—4 eV); 4) the absorptivity of other components is not important and does not make excitation difficult; 5) the strongly luminescing components are not excited (they can be excited only by energy transfer); 6) the

excitation is of the "dark" type—therefore, the usual selection rules do not apply and the "forbidden" levels may be populated effectively. In particular, if photo-excitation were used it would be very difficult, or altogether impossible, to investigate the transfer of energy from a weakly luminescing donor (ketone) to a strongly luminescing activator: not only the ketone but also the anthracene would be excited because both absorb in the same region of the spectrum. In the activated chemiluminescence, the excited states are generated chemically in darkness and the strongly luminescing components can be excited only by energy transfer, which has been investigated in [22].

The obvious disadvantage of the method is its specificity—not every compound can be synthesized in such a way that it would be produced in the excited state in the synthesis reaction. Other features of the method, which may be undesirable, are the need to have certain reagents present and the low intensity of luminescence.

V. CONCLUSIONS

The information presented here shows that investigations of chemiluminescence already represent an extensive, interesting, and rapidly developing branch of science at the interface of physics and chemistry. The phenomenon of chemiluminescence is characterized by a number of relationships, which apply to any reaction (cf. Sec. 1). On the other hand, chemiluminescence is a very specific effect and the transformation of chemical into optical energy may take place in different ways in different reactions. Moreover, in the same reaction, more than one product may be excited and the excited products may emit in one or more different spectral regions. The nature of the exciting reaction itself may differ in different chemical systems.

These characteristics are not always allowed for in the investigations of chemiluminescence. For example, some authors have developed certain ideas on the radical nature of chemiluminescent reactions.[87,154] Moreover, the existence of luminescence has been suggested as a proof of the participation of radicals in a reaction,[83,130] and it even has been suggested that the chemiluminescence in the short-wavelength (blue and shorter wavelengths) region can only be the result of reactions involving two free radicals.[87] It is true that the effective transformation of chemical energy into radiation is more likely and more frequently met in the recombination of radicals. Nevertheless, it would be wrong to reject the possibility of excitation in reactions other than recombination. For example, bright flashes have been observed on the admission of molecular fluorine into a jet of H_2 or CH_4.[45] In these reactions, we have the following elementary acts

$$H + F_2 \rightarrow HF + F + 100 \text{ kcal/mole,}$$
$$CH_3 + F_2 \rightarrow CH_3F + F + 70 \text{ kcal/mole,}$$
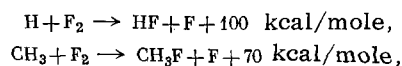
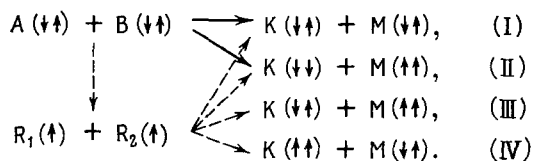These are sufficiently exothermal but they involve only one free radical as the initial reagent.

In the present author's opinion, there are only two conditions necessary for the appearance of chemiluminescence:

a) the reaction should be sufficiently exothermal (law of conservation of energy);

b) the product should have a suitable energy level from which radiation is reasonably probable.

The excitation carrier in solutions is the electron state because the vibrational excitation is lost rapidly. The structure of the spectrum is governed by the luminescent properties of the excited state and not by the amount of energy evolved (this amount should, of course, correspond to the emitted quantum of light).

In those cases when the products of an exothermal reaction have a triplet level, the excitation of this level is favored by the fact that in the majority of molecules such a level lies low and requires less energy than an excited singlet level. The problem of the multiplet nature of an excited particle can sometimes be solved uniquely on the basis of the law of conservation of the total spin of a system (Wigner's rule). However, applying Wigner's rule, we must bear in mind that it is applicable to an elementary act and not to the whole reaction.

For example, if the reaction between saturated molecules A and B consists of one elementary act, then both products K and M should be obtained either in a singlet or in a triplet state (combinations I and II):

$$A\,(\uparrow\downarrow) + B\,(\uparrow\downarrow) \longrightarrow K\,(\uparrow\downarrow) + M\,(\uparrow\downarrow), \quad (I)$$
$$K\,(\uparrow\downarrow) + M\,(\uparrow\uparrow), \quad (II)$$
$$K\,(\uparrow\downarrow) + M\,(\uparrow\uparrow), \quad (III)$$
$$R_1\,(\uparrow) + R_2\,(\uparrow) \longrightarrow K\,(\uparrow\uparrow) + M\,(\uparrow\downarrow). \quad (IV)$$

If the reaction is of the radical type, other combinations (III and IV) are also possible. In view of this, it is premature to draw conclusions on the triplet nature of the excited states in the oxidation of luminol[154] and oxalyl chloride.[91]

A reaction may violate Wigner's rule, because this rule is not very rigorous. Then, the excitation process should have low probability (low yield). Conversely, if the experimentally determined yield of chemiluminescence is high, it can hardly be expected that the elementary excitation would involve a change of the multiplet nature. That is why it is important to measure correctly the quantum yield in investigations of the mechanism of chemiluminescence. In this connection, the following points should be made.

1. In the determination of the chemiluminescence yield, the intensity of luminescence should be referred not to the reaction as a whole, but to the rate of formation of the luminescent product.

2. The process of chemiluminescence takes place in two stages and, consequently, the total luminescence yield depends on the excitation yield η_P^{exc} and the luminescence yield η_P. These quantities have basically different physical meanings and depend in different ways on the molecular structure, environment, experimental conditions, etc.

The majority of chemiluminescent reactions are oxidation reactions. This is probably because the products of oxidation reactions (ketones, aldehydes, O_2) have low-lying energy levels which can be relatively easily populated in a reaction (i.e., the yield η_P^{exc} is relatively high); moreover, oxygen-bearing compounds luminesce relatively strongly in the visible part of the spectrum (i.e., the yield η_P is relatively high).

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