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CHEMILUMINESCENCE AND THE KINETICS OF CHEMICAL REACTIONS

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I. INTRODUCTION

Chemiluminescence — the emission of light accompanying chemical reactions — is closely connected with the kinetics and the mechanism of the reaction.

The appearance of excited states in a reaction zone is due to the occurrence of exothermic elementary acts. The measured intensity of emission is proportional to the rate of the elementary process in which energy is evolved, and hence is related to the kinetic parameters of the reaction. Investigation of the kinetics, the temperature dependence, and the spectra of the emission may give much valuable information for an understanding both of the reaction mechanism and of the actual phenomenon of chemiluminescence — of the ways in which chemical energy is transformed into radiation.

It must be emphasised that a study of chemiluminescence divorced from the mechanism of the corresponding reaction can hardly provide a fruitful approach. For example, the weakening of emission accompanying the introduction of a new component into the reaction mixture can be equally well explained by its retarding effect on the reaction velocity or by its quenching action on excited states which appear at the same rate as before. In the absence of information on the rate of the chemical reaction and of the influence of the additive on it, no choice can be made between these fundamentally different effects.

The present review surveys the relationship between the chemiluminescence and the kinetics of reactions. From the considerable number of papers on chemiluminescence, those have been selected which report either the investigation of chemiluminescence in reactions whose mechanism has been reliably established or the parallel study of a reaction by chemiluminescence and chemical kinetic methods.

Special attention has been paid to the prospects for using chemiluminescence as a method for the quantitative investigation of reaction kinetics.

The main information has been divided into three parts — (1) gas-phase reactions (hot and cold flames, reactions of atoms obtained in high concentrations from electric discharges), (2) liquid-phase reactions (oxidation of cyclic hydrazides and of acridine compounds) accompanied by bright chemiluminescence, and (3) reactions accompanied by very weak chemiluminescence, which do not differ fundamentally from the previous reactions, but comprise a wide range of both scientific and practical interest, and therefore are discussed as a separate group.

II. CHEMILUMINESCENCE OF FLAMES

The intensity of the emission from many flames exceeds the equilibrium value corresponding to the temperature of the flame. In particular, the glow from cold and dilute flames is purely chemiluminescent. The radiation from low-temperature flames is to a greater or lesser extent chemiluminescent[1,2]. The non-equilibrium character of the radiation can be shown by comparing its absolute intensity with the intensity of the radiation from a black body having the same temperature as the flame. Thus according to Kondrat'ev[1] the intensity of the radiation from an oxygen–hydrogen flame at 10 mmHg and 1000°K exceeds the equilibrium value by a factor of 10^{12}, while the corresponding factor for the $2CO + O_2$ flame at 100 mmHg and 1400°K is 10^{10}.

The character of the radiation can be assessed also from measurements of the intensity distribution in the emission spectrum. The non-equilibrium character of radiation is indicated by a difference between the true temperature of the flame and the rotational temperature of individual species: in the oxygen–acetylene flame at 1 atm, for example, the true temperature is 3400°K, while the rotational temperature of hydroxyl is 5400°K, and that of C_2 is 4700°K.[3] Finally, departures from equilibrium can

be assessed from the characteristic quenching of luminescence with increase in the pressure of the reactants or on the introduction of inert gases. Quenching phenomena have been observed, for example, in the hydrogen and carbon monoxide flames[1].

Flame emission spectra usually comprise one or more band systems observed on a background of a continuous spectrum. The source of the energy responsible for the chemiluminescence is usually the recombination (or disproportionation) of atoms and free radicals, in which a large amount of energy, equivalent to quanta in the visible and ultraviolet regions of the spectrum, is evolved at once, in a single act. Therefore measurements of chemiluminescence in flames give information on the reactivities of atoms and free radicals, their concentrations, and their concentration distributions in the flame and in the combustion products.

The use of chemiluminescence data in the study of reaction kinetics in flames and combustion products is based on the existence of proportionality between the emission intensity I and the rate w of the chemical process resulting in chemiluminescence:

$$I = \eta_{ch}\omega, \quad (1)$$

where η_{ch} is a proportionality coefficient representing the quantum yield of the radiation. In general η_{ch} may depend on the temperature and on the composition of the mixture in which reaction is occurring. The principal cause of variation in the light yield is change in the composition of the mixture. The coefficient η_{ch} may vary both as a result of strengthening or weakening of quenching processes and as a result of energy transfer processes, which may affect the nature of the luminescent species. The temperature variation in the light yield is usually small, and is due mainly to the temperature dependence of the probability of radiationless transitions. The kinetics can be measured by various methods based on chemiluminescence:

(a) Measurement of intensity of emission in a chemiluminescent reaction occurring in the system.

(b) Measurement of intensity of emission from an added luminescent substance. In this case chemiluminescent reactions may be altogether absent in the actual system investigated. The chemiluminescence of the added substance (activator) arises from energy transfer.

(c) Measurement of intensity of emission occurring on addition of a substance which enters into a chemiluminescent reaction with one of the components of the system. In this case, too, chemiluminescent reactions may be absent from the actual system investigated.

All these chemiluminescent methods are used in kinetic investigations of flame reactions. The latter two methods are employed especially frequently.

1. Chemiluminescent Reactions with Additives

The flame and the products of the combustion of hydrogen form the subject of most quantitative investigations of chemiluminescence. The reaction involves O and H atoms and the OH radical. The application of chemiluminescent methods makes it possible to measure relative and absolute concentrations of these species and their distribution in the combustion products, and to obtain rate constants for their recombination.

Concentration distributions of H atoms in the hydrogen flame and in the reaction products have been measured, for example, from the emission arising on the introduction of copper into the flame. A bright emission band due to CuH is recorded, its intensity I_{CuH} at $\lambda = 4280$ Å being proportional to the concentration of H atoms[4,5]. Reid and Sugden have shown[6] that the constant k' in the expression $I_{CuH} = k'[H]$ is independent of temperature. Therefore $[H]/[H]^\circ = I_{CuH}/I^\circ_{CuH}$ (I°_{CuH} being the intensity of emission at the concentration of H atoms chosen as standard), and relative concentrations of H atoms can be measured by I_{CuH}. These measurements can be converted to absolute concentrations provided that [H] is measured at one point by some absolute method. According to Sugden's data[7] the equilibrium

$$OH + H_2 \rightleftarrows H_2O + H \quad (2)$$

is rapidly established in the products of the combustion of hydrogen. This makes it possible to determine the concentration of OH radicals and their distribution in the products of the hydrogen flame from known values of [H] and the equilibrium constant of process (2). In this way the following recombination rate constants have been obtained[5]

$$H + OH + H_2O \rightarrow H_2O + H_2O \quad k_{1650} = 1.5 \times 10^{-30}\ cm^6\ s^{-1},$$
$$H + H + H_2O \rightarrow H_2 + H_2O \quad k_{1650} = 6 \times 10^{-32}\ cm^6\ s^{-1}.$$

The addition of halogens to hydrogen flames having a high fuel content results in continuous emission in the visible region, due to the reaction $H + X \rightarrow HX + h\nu$, where X is a halogen atom[8]. This emission resembles the continuum of the hydrogen flame arising in the reaction $H + OH \rightarrow H_2O + h\nu$.[9] The weak continuum emitted in the visible region when an alkali metal M is added to a hydrogen flame has an intensity proportional to [OH][M]. The continuum probably arises[10] in the reaction $M + OH \rightarrow MOH + h\nu$. In all these cases the emission intensity can be used to determine the relative concentration of H atoms and OH radicals in different parts of the flame and combustion products. These data can be used also to calculate the distribution of oxygen atoms, since the equilibrium

$$H_2 + O \rightleftarrows H + OH$$

is rapidly established in the flame.

A method suggested by Gaydon[11] has often been used recently to determine the concentration of atomic oxygen. It is based on measurement of the intensity of the yellow-green glow in the reaction.

$$NO + O \rightarrow NO_2 + h\nu. \quad (3)$$

In Gaydon's work this method was employed only qualitatively, the emission serving as an indicator of atomic oxygen. The work of Karmilova and Kondrat'ev[12], who made absolute measurements of the intensity of the yellow-green emission of NO_2, showed that the intensity is a quantitative measure of the concentration of atomic oxygen in the CO flame. The concentration of O atoms was close to the equilibrium values in flames having a temperature above 2600°K; at lower temperatures it exceeds the equilibrium value. The possibility of the quantitative use of reaction (3) to measure relative and absolute concentrations of atomic oxygen in flames has been confirmed by later work. Thus James and Sugden[13] have shown that the intensity of the emission from the combustion products of hydrogen to which nitric oxide has been added is proportional to [NO] and to the concentration of O atoms, the latter being calculated from the equilibrium constants.

Measurements of the absolute light yield in reaction (3) taking place in the combustion products of the hydrogen flame have been used[14] to evaluate the rate constant of reaction (3)†. The value of 2×10^{-18} cm^3 s^{-1} for the rate constant agrees well with the value obtained by Kaufman[15] using a different method.

2. Emission from Luminescent Additives

Emission lines due to various metal impurities can be observed in the spectra of many flames. Gaydon and Wolfhard[3] put forward the hypothesis that the excitation of metal atoms in flames is effected by the energy released by the recombination of atoms and free radicals. The number of excited impurity atoms may correspond to the temperature of the flame, but can also considerably exceed the equilibrium value. This is especially characteristic of low-temperature and highly dilute flames, in which the concentration of atoms and free radicals far exceeds the equilibrium value. Measurements of the emission intensity from a metal impurity can be used as a quantitative method for studying the kinetics of reactions involving atoms and free radicals. Thus the decay of the chemiluminescence of metallic sodium has been used[16] to measure the kinetics of the recombination of atomic hydrogen at 1072°K in the products of combustion from a mixture of $H_2 + O_2 + N_2$. The absolute concentration of H atoms was measured from the rate of their reaction with D_2O or D_2.

In the products of combustion, hydrogen is removed by the reactions

$$H+H+M \rightarrow H_2+M, \quad (4)$$

$$H+OH+M \rightarrow H_2O+M. \quad (5)$$

If M = Na, both reactions result in the formation of excited sodium atoms emitting a resonance line. The probability of the excitation of sodium in these reactions is of the order of unity[17].

Since the concentrations of H atoms and OH radicals are balanced by the occurrence of process (2), the decrease in emission intensity can be used to measure the relative concentration of H atoms, although they immediately disappear by the two reactions (4) and (5). The time variation in the emission intensity is almost independent of the relative proportions of N_2, H_2, and H_2O, which are evidently equally effective as third bodies.

Analogous measurements can be made with other metals, e.g. thallium and lead, the resonance emission of which is excited in the processes[18]

$$H+H+Tl \rightarrow H_2+Tl^* \quad (\lambda=535\ m\mu m),$$
$$H+OH+Pb \rightarrow H_2O+Pb^* \quad (\lambda=405.8\ m\mu m).$$

New excitation reactions occur when halogens X_2 and metal vapours are introduced simultaneously into a hydrogen flame[19]

$$H+X+M \rightarrow M^*+HX \quad (X=Cl, Br).$$

In these processes the heat of reaction can be almost completely transformed into the energy of excitation of the metal atom. Thus the heat of reaction of H + Cl (102 kcal × × mole^{-1})‡ is almost completely utilised for the excitation of a lead atom (excitation potential 100 kcal). Measurements of the emission of metal atoms in reactions between hydrogen and halogen atoms can also be used in kinetic investigations.

III. REACTIONS OF NITROGEN, OXYGEN, AND HYDROGEN ATOMS

Methods analogous to those described above are used also to investigate non-flame reactions of nitrogen, oxygen, and hydrogen atoms. In this case the atoms are usually obtained in electric discharges, and their reactions are investigated in a flow apparatus from the distribution of emission intensity along the reaction tube.

1. Reactions of Atomic Nitrogen

It was observed in 1900 that nitrogen which has passed through an electric discharge exhibits a yellow afterglow[20], associated with the reactions[21]

$$N(^4S)+N(^4S)+M \rightarrow N_2(^5\Sigma_g^+)+M \text{—rate-determining stage},$$
$$N_2(^5\Sigma_g^+)+M \rightarrow N_2(B^3\Pi_g)+M,$$
$$N_2(B^3\Pi_g) \rightarrow N_2(A^3\Sigma_u^+)+h\nu \text{ — chemiluminescence}.$$

Simultaneous recording of the emission intensity and mass-spectrometric measurement of the concentration of atomic nitrogen[21] have shown that $I = \alpha[N]^2$, the coefficient α being proportional to the pressure of N_2. This shows that the luminescence arises from a termolecular recombination. Measurement of the absolute intensity of the glow has yielded an estimated rate constant for the recombination of N of 2×10^{-33} cm^6 s^{-1}.[21] A more accurate value for the constant — 1.72×10^{-32} cm^6 s^{-1} — has been obtained by measuring the distribution of emission intensity along the tube through which the mixture of atomic and molecular nitrogen from the electric discharge is passed[22].

The absolute concentration of nitrogen atoms was determined by a method of "chemiluminescent titration"[23] with NO. The nitric oxide enters from a small volume through a calibrated orifice into the tube along which the jet from the discharge is passing. The very rapid reaction N + NO → N_2 + O takes place, and a new chemiluminescent reaction O + NO → $NO_2 + h\nu$ appears. The yellow glow of the nitrogen does not immediately vanish, but a yellow-green luminescence, associated with the reaction of atomic oxygen, appears. Since the vessel containing the nitric oxide has a small volume, the rate of escape of NO drops rapidly, and when its amount becomes insufficient and N atoms remain, a new blue-violet luminescence appears, associated with the reaction[22,24]

$$N+O+M \rightarrow NO(A^2\Sigma^+, B^2\Pi)+M,$$
$$NO(A^2\Sigma^+, B^2\Pi) \rightarrow NO+h\nu \ (\beta \text{ and } \gamma \text{ bands}).$$

At the instant of appearance of the blue-violet glow, the quantity of NO molecules which have entered is equal to the number of N atoms. The presence of NO in the vessel is measured at this point, the flow of NO is determined from a calibration curve, and in this way the concentration of nitrogen atoms is obtained. The "titration" takes a few minutes.

2. Reactions of Atomic Oxygen

The recombination of atomic oxygen

$$O(^3P)+O(^3P)+M \rightarrow O_2+M \quad (6)$$

† The hydroxyl concentration was determined by the method of ultraviolet absorption[1]. The concentration of O atoms was calculated from values of the equilibrium constant of the reaction $2OH \rightleftharpoons H_2O + O$.

‡ Henceforward we shall write kcal instead of "kcal mole^{-1}".

is not chemiluminescent. Nevertheless, the reaction velocity and the rate constant can be measured by chemiluminescent methods. If small amounts of NO are introduced into a jet containing oxygen atoms, a quite bright emission is produced, whose intensity is proportional to the concentration of atomic oxygen[25-28]. At the same time, the reaction $NO + O \rightarrow NO_2$ is slow at low NO concentrations, in comparison with other reactions of O atoms, and it has hardly any effect on the concentration of the latter[23]. The nitrogen dioxide which is formed reacts very rapidly with O atoms to regenerate NO:

$$O+NO_2 \rightarrow O_2+NO. \quad (7)$$

Reaction (7) is used for the chemiluminescent "titration" of O atoms. A gradually increasing flow of NO_2 is admitted to the jet. As a result of the rapid reaction (7), [O] decreases, while [NO] increases. The emission intensity, which is proportional to the product [O][NO], passes through a maximum. With further increase in the flow of NO_2, the intensity falls rapidly. The end-point corresponds to complete disappearance of luminescence from the tube. At this point the supply of NO_2 is equal to the concentration of O.[29] In a variant of this method[30], which probably yields more accurate results, measurements of the intensity distribution along the tube and the application of chemiluminescent titration enable the rate constant of reaction (6) to be determined[29,30]. The technique shows promise for the quantitative investigation of other reactions of atomic oxygen. Thus the kinetics of the consumption of oxygen atoms has been examined[29] in the presence of H_2, O_2, N_2, Ar, CO_2, CO, N_2O, C_6H_6, SO_2, $Fe(CO)_5$, H_2O, O_3, C_2H_4, Cl_2, and Br_2. Results obtained by chemiluminescent method have been discussed in detail in a recent review by Kaufman[31].

3. Reactions of Atomic Hydrogen

The recombination of atomic hydrogen catalysed by nitric oxide is accompanied by luminescence in the red and near infrared regions of the spectrum, due to emission by excited HNO molecules[32-34]:

$$H+NO+M \rightarrow HNO^* + M \text{ — rate-determining stage}, \quad (8)$$

$$H+HNO \rightarrow H_2+NO. \quad (9)$$

Radiation from HNO* is observed also in the rapid reaction[33]

$$H+NO_2 \rightarrow OH+NO.$$

The kinetics of the catalysed recombination has been studied[33,34] from the intensity of the red luminescence in a low-pressure (1–2 mmHg) jet. The rate constant of reaction (8) and the intensity depend substantially on the nature of the third species M, where $I \propto [H][NO]$. From the intensity distribution along the jet and calorimetric measurements of the concentration of hydrogen atoms, the rate constant of reaction (8) was found to be 1.3×10^{-32} cm^6 s^{-1} (with M = H_2).

This reaction may perhaps be used in the future as an indicator of atomic hydrogen, and employed to study reactions of the latter with various molecules, as has been done for the reactions of atomic oxygen.

IV. INFRARED CHEMILUMINESCENCE IN THERMAL REACTIONS

The distribution of energy among the products of exothermic reactions is not the equilibrium distribution. Reference may be made, for example, to a series of results obtained by M. Polanyi and his coworkers, who investigated the reactions of alkali-metal vapours with halogens, as well as with organic and inorganic halogen compounds. The kinetics and the characteristics of the chemiluminescence in these reactions have been discussed in detail in several review articles and monographs[2,35,36]. Here we shall consider only those facts which indicate the formation in these reactions of excited species, present in vibrationally excited or metastable states. The simplest reaction — that between the vapours of sodium and a halogen X_2 — occurs according to the scheme

$$Na+X_2 \rightarrow NaX+X, \quad (10)$$

$$X+Na_2 \rightarrow NaX'+Na, \quad (11)$$

$$NaX'+Na \rightarrow NaX+Na^*, \quad (12)$$

$$Na^* \rightarrow Na + h\nu, \quad (13)$$

where NaX′ is an excited molecule. The main evidence for the formation of NaX′ molecules and the excitation of sodium in reaction (12) is based on an investigation of the quenching of chemiluminescence by foreign gases, which showed that the chemiluminescence was extinguished considerably more strongly than was the fluorescence of sodium. If the reaction is carried out in a flow apparatus, the zone of maximum emission intensity is displaced in the flow direction. It is interesting that in individual cases the heat of reaction is almost completely converted into excitation energy; for example, emission of the 0.589 μm (48.5 kcal) sodium resonance line is observed in the reaction $Na_2 + I \rightarrow NaI + Na$, the heat of which reaction is 49.5 kcal.

The formation of vibrationally excited molecules in a chemical process was first detected spectroscopically by McKinley et al.[37] for the reaction of hydrogen atoms with ozone $H + O_3 \rightarrow OH' + O_2$. The reaction was carried out at 0.2 mmHg in a reaction vessel comprising two coaxial tubes. A stream of ozone from the inner tube entered an atmosphere of partly dissociated hydrogen which had passed through a discharge tube. A red glow appeared at the outlet from the inner tube, produced by vibrationally excited OH radicals, whose spectrum was recorded on a photographic plate. The spectrum contained bands corresponding to transitions from vibrational levels right up to the level of quantum number 9. The energy of this highest level (75 kcal) is close to the heat of reaction (78 kcal). Vibrationally excited molecules were detected also in a large number of photochemical and thermal reactions. By the method of flash photolysis, vibrationally excited species have been obtained, for example, in the reactions[38-40] (the numerals in parentheses indicate the highest observed vibrational level)

$$O+NO_2 \rightarrow O_2\,(8)+NO, \quad Br+O_3 \rightarrow BrO\,(4)+O_2,$$
$$O+Cl_2O \rightarrow O_2\,(8)+ClO, \quad O+NH_3 \rightarrow OH\,(2)+NH_2,$$
$$O+O_3 \rightarrow O_2\,(17)+O_2, \quad O+CH_4 \rightarrow OH\,(2)+CH_3,$$
$$Cl+O_3 \rightarrow ClO\,(5?)+O_2, \quad O+HCl \rightarrow OH\,(2)+Cl.$$

The concentrations of excited species are large here, and they are identified from their absorption spectra.

A series of investigations of infrared chemiluminescence has been made by J. C. Polanyi and his coworkers[41-45], who observed from the emission spectra the formation of vibrationally excited molecules, e.g. in the reactions

$$H+NO \rightarrow HNO' \quad H+Br_2 \rightarrow HBr'+Br,$$
$$H+Cl_2 \rightarrow HCl'+Cl \quad H+NOCl \rightarrow HCl'+NO.$$

It is seen from the above equations that, in reactions of atoms with triatomic molecules, the heat of reaction is not uniformly distributed among the products. Most of the

energy — and in isolated cases the whole of it — is concentrated on the bond which is formed. Only in the reaction H + NOCl were both species NO and HCl vibrationally excited. Even in this case, however, the distribution of energy was non-uniform: the emission of the NO constituted only a few per cent of that from the HCl.[45]

All the reactions quoted in the present Section were formerly regarded as elementary. However, the formation of excited products in different vibrational states shows that this view is an oversimplification. In fact, the measured rate constant represents the sum of the rate constants of reactions leading to products which are present in various vibrational states. Therefore investigation of the energy spectrum of the resulting products is of exceptional interest for the construction of a quantitative theory of the elementary acts in chemical processes. The first work on these lines has been undertaken recently. In the H + O_3 reaction it has been concluded, from measurements on the distribution of OH among vibrational levels with an initial pressure of 2–5 mmHg, that the rate constants for the formation of different excited states of OH are approximately the same[46]. However, this conclusion cannot be regarded as final, and requires further verification. Thus it has been shown[44,45,47,48] for the reactions H + NOCl and H + Cl_2 that the distribution of HCl among vibrational levels depends significantly on the initial pressure and the partial pressure of HCl. At higher pressures (0.1–0.2 mmHg for H + Cl_2 and 1–2 mmHg for H + NOCl) the HCl exhibits an approximately Boltzmann distribution among vibrational levels, and the relative rate constants for the formation of HCl molecules at a given vibrational level are closely similar for the two reactions, in spite of the differences in the nature of the reactant molecules (the Cl_2 molecule being non-polar, while NOCl is polar) and in the heats of reaction. These results can be explained by the fact that, at higher pressures, the original distribution of energy among vibrational levels is strongly distorted by secondary processes involving the redistribution of energy.

At pressures of around 0.01 mmHg in the H + Cl_2 system, emission disappears from levels located above $v = 5$ (at higher pressures the level $v = 6$ was observed). In the H + NOCl system no emission is observed from the levels $v = 8$ and $v = 9$, which had been observed at higher pressures. The distribution among vibrational levels becomes markedly different from the Boltzmann distribution, and differs greatly for the two systems. Under these conditions reaction is most rapid to form HCl molecules in their lowest vibrational states; in the H + Cl_2 reaction, for example, the rate of formation of HCl($v = 3$) exceeds that of HCl($v = 5$) by a factor of approximately 35. The highest vibrational levels are excited at higher pressures probably as a result of the redistribution of energy.

V. LIQUID-PHASE OXIDATIONS ACCOMPANIED BY BRIGHT CHEMILUMINESCENCE

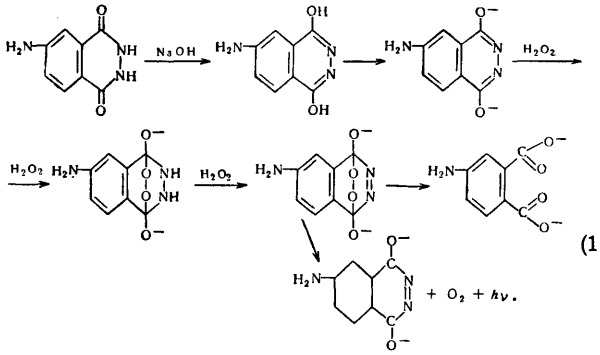
1. Oxidation of Cyclic Hydrazides

The chemiluminescence accompanying the oxidation of 5-amino-1,2,3,4-tetrahydro-1,4-dioxophthalazine (Luminol) with hydrogen peroxide in alkaline medium was first studied by Albrecht in 1928.[49] The luminescence was long-lived, and so intense that it could be observed with the naked eye. It has also been discovered that bright chemiluminescence accompanies oxidation of the hydrazides of benzenesulphonic[50], pyridinecarboxylic[51], aromatic, and aliphatic[52,53] acids. Several regularities have been observed in the dependence of the intensity of chemiluminescence on the structure of the hydrazides. However, many authors have based their conclusions on the results of visual observations or measurements with instruments of low sensitivity, and therefore their conclusions concerning the absence of chemiluminescence in the oxidation of a particular compound cannot be regarded as final.

Experiment has shown that several hydrazides of phthalic acids, and especially of aminophthalic acids, possess most long-lived and intense luminescence. According to Sveshnikov[54] the brightness of the emission at Luminol concentrations of 10^{-5}–10^{-3} g cm^{-3} is 3×10^{-7} to 2×10^{-6} stilb with a layer 1 cm thick. Ordinary photometers can be used to study such reactions. Therefore the oxidation of Luminol in alkaline medium, with and without a catalyst present, has become a kind of model reaction for the study of chemiluminescence in the liquid phase. The oxidants used have been hydrogen peroxide, peroxosulphates[1], permanganate[55], $[CoCl_2(NH_3)_4]Cl$,[56] and other compounds[57]. Catalysts of various types considerably intensify the chemiluminescence[57]. Many workers have attempted to elucidate the mechanism of these reactions, by studying the effect of the nature and position of substituents in the benzene and hydrazide rings on the intensity and spectral region of the emission[58–69]. Several reaction schemes have been suggested for the oxidation of [hydrazides of] phthalic acids with hydrogen peroxide in alkaline medium, which result in the emission of radiation.

Thus Albrecht[49], Tamamushi[70], and Weber[71] assumed that the oxidation of Luminol involves the intermediate formation of a diimide and an excited dilactam form of the hydrazide. A similar hypothesis was put forward by Caen[72] for the oxidation of Rimifon (the hydrazide of isonicotinic acid). However, existence of the diimide was not confirmed experimentally.

Parker and Harris[73], and later Drew and Garwood[63,64,74], suggested that the Luminol molecule adds on a molecule of H_2O_2 to form a peroxide. The oxygen bridge is eliminated, and the epidioxide molecule converted into an excited Luminol molecule, which is responsible for the chemiluminescence:



(14)

Several pieces of evidence in support of this hypothesis were given[59,63]. Ojima[75] suggested a similar mechanism for the luminescence of Luminol in the presence of copper salts.

Babko and Lukovskaya[76] showed by the method of isomolar series that copper forms a 1 : 1 complex with

Luminol, and the H_2O_2 molecule adds on in turn in this complex, forming a new complex responsible for the emission.

Many workers have shown[63,68,73,77-80] that with variation in the H_2O_2 concentration the initial intensity passes through a maximum. However, different authors give different relative concentrations of Luminol and hydrogen peroxide corresponding to this maximum, covering the range 1–50 molecules of H_2O_2 per molecule of Luminol.

Especially detailed kinetic investigations were made by Sveshnikov[54,77-79], who used a Fabry–Gelhof photometer to study the time variation of emission intensity in the oxidation of Luminol in alkaline medium at 52°C and the effect of the H_2O_2 and alkali concentrations on the intensity. The time curves show that, within the limits of experimental error, the emission intensity I is proportional to the Luminol concentration, while the kinetics of the variation in intensity remains unchanged when the Luminol concentration is diminished by a factor of 100. The rate of change of I increases as the concentration of the hydrazide decreases. According to Sveshnikov, the chemiluminescence corresponds to some secondary reaction which is of the first order with respect to the Luminol concentration. His experimental results support the hypothesis of Drew and Garwood, and are at variance with the Albrecht–Tamamushi scheme, which requires a quadratic dependence of I on the Luminol concentration.

Bernanose[81] showed that, when Luminol is oxidised with sodium hypochlorite and hydrogen peroxide, the luminescence diminishes with time according to an exponential law. Several workers, who have investigated the kinetics of the chemiluminescence of Luminol in the presence of catalysts[71,82-87], have observed the same law for the time variation of the emission. It may be surmised that the same elementary act, perhaps the unimolecular breakdown of Luminol peroxide, is responsible for the chemiluminescence in all cases.

The brightness of the chemiluminescence of Luminol depends significantly on the pH of the medium, reaching a maximum at pH 10–11. Several explanations have been suggested for this phenomenon. Some workers[66,81] consider that the pH influences an equilibrium between two forms — luminescent and non-luminescent — of Luminol. Babko and Lukovskaya[88] assume that the effect of pH is linked with the dissociation of Luminol. Erdey[89], who studied the decomposition of hydrogen peroxide in alkaline medium, showed that the ion HOO^- was formed as active intermediate, the rate of decomposition of H_2O_2 being a maximum at pH 12. He postulated that this ion adds on to a molecule of the luminous substance to form a peroxide, whose decomposition causes the chemiluminescence (Drew and Garwood's mechanism). From this point of view the presence of an extremum in the pH dependence of the rate of decomposition of H_2O_2 may be one reason for the appearance of a maximum on the chemiluminescence intensity curve.

Thus, although the mechanism of the chemiluminescence of Luminol has not been finally established, Drew and Garwood's scheme (14) seems the most probable.

Besides the above mechanisms of "ionic" type, several investigators suggest "radical" mechanisms for the oxidation of Luminol with hydrogen peroxide[87,90]. These hypotheses are based on theories of the chain decomposition of hydrogen peroxide in acid medium, and also the observed[54,64,83,87,90] quenching action of inhibitors of radical reactions — quinol, Metol, cysteine, etc. — on the chemiluminescence of Luminol, which was restored as the inhibitor was consumed. These schemes do not agree with Sveshnikov's kinetic results, since they presuppose that the intensity of chemiluminescence depends on higher powers of the concentration of the luminescent substance, nor with Erdey's conclusions concerning the formation of HOO^- ion in alkaline medium. Thus further kinetic and spectroscopic study of the chemiluminescent reaction of Luminol is required in order to establish the mechanism of the luminescence accompanying this process.

Although the mechanism of chemiluminescent oxidation has not yet been established, the pH dependence of the bright luminescence of Luminol is widely used in analytical chemistry. Luminol is employed to detect H_2O_2,[91] $CuCl_2$, Br_2, $KMnO_4$, NH_3,[92] and poison gases[53], for the quantitative determination of H_2O_2,[94] copper[76,88,94], and several organic compounds[94], and also as an acid–base indicator[95].

2. Oxidation of Lucigenin

The bright green luminescence accompanying the oxidation of alkaline *NN'*-dimethylbiacridinylium solutions with hydrogen peroxide was first investigated in detail by Gleu and Petsch[96,97] in 1935. They gave the name "lucigenin" (generating light) to the compound.

As in the case of Luminol, several hypotheses have been put forward to explain the mechanism of the luminescence of lucigenin. Only hydrogen peroxide and oxygen produce chemiluminescence in alkaline solutions of this compound, and the resulting spectrum is identical with its fluorescence spectrum.

Tamamushi and Akiyama[98,99] consider that the oxidation of lucigenin with oxygen involves formation of a diradical, 10,10'-dimethyl-9,9'-biacridinyl, which on addition of O_2 forms lucigenin peroxide. Under the influence of the previously formed H_2O_2, this peroxide is converted into a dicarbinol base, which is in an excited state and is responsible for the luminescence.

Gleu and Petsch[96] postulate a reaction scheme in which lucigenin oxide (10,10'-dimethyl-9,9'-biacridinylidene oxide) is directly responsible for the emission, while the intensity of chemiluminescence is proportional to the first power of the lucigenin concentration.

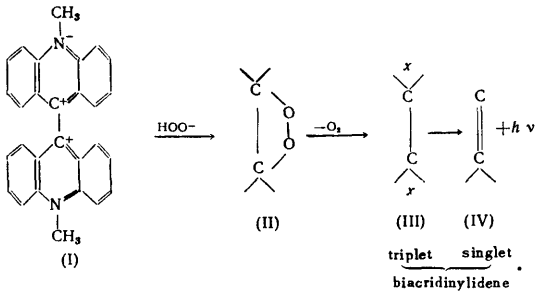
Totter et al.[100] assume that the oxidation of lucigenin involves the intermediate formation not of an oxide or a peroxide but of 10,10'-dimethyl-9,9'-biacridinylidene, followed by a monocarbinol base, which is responsible for the luminescence.

Erdey[101] considers that in alkaline medium the lucigenin molecule reacts with the HOO^- ion formed on decomposition of H_2O_2, to yield lucigenin peroxide (similarly to the scheme of Gleu and Petsch).

Grigorovskii and Simeonov[102], having synthesised several derivatives of lucigenin, showed that lucigenin oxide and 10,10'-dimethyl-9,9'-biacridinylidene are able to emit a bright yellow-green chemiluminescence in alkaline medium under the influence of hydrogen peroxide, whereas the monocarbinol base does not emit light under these conditions.

Very interesting spectroscopic investigations were made by Karyakin[103], who studied the chemiluminescence, phosphorescence, and fluorescence spectra of lucigenin brom-

ide (I), *NN'*-dimethylbiacridinylidene oxide (II), and *NN'*-dimethylbiacridinylidene (III) (see Table). Since the chemiluminescence spectra of aqueous solutions of lucigenin and of lucigenin oxide are not identical, Karyakin considers that the oxide is not an intermediate product in the oxidation of lucigenin, and that the emission from the oxide represents an independence process. The chemiluminescence spectra are similar to the phosphorescence spectra. This implies that an excited triplet level is responsible for the chemiluminescence. Karyakin[103] and Erdey[104] suggest an emission mechanism for lucigenin comprising the stages — (1) H_2O_2, or most probably the HOO^- ion, reacts with the starting material to form a transannular epidioxide; (2) the latter decomposes thermally with the evolution of O_2 and formation of the corresponding diradical (triplet) state; and (3) the diradical passes into the ground state, emitting a quantum of light:



On addition of a catalyst, lucigenin peroxide (II) decomposes to form an excited methyloxoacridine, which emits a blue glow.

In a study of the kinetics of the chemiluminescence of lucigenin and the dependence of the intensity of chemiluminescence on the concentrations of lucigenin, H_2O_2, and alkali[54,79], Sveshnikov showed that, whereas with Luminol the curve for the time variation in the intensity represents a complicated process, in the case of lucigenin the curves follow exactly an exponential law. The kinetic curves show that the rate of variation in chemiluminescence increases with decrease in the concentration of the substance, as in the case of Luminol. This confirms the hypothesis that both lucigenin and Luminol inhibit the decomposition of H_2O_2. Furthermore, Sveshnikov showed that, with lucigenin too, the dependence of the initial intensity of chemiluminescence on the concentration of the substance in the presence of large excesses of H_2O_2 and NaOH is not quadratic. Moreover, the strengthening of chemiluminescence with increase in lucigenin concentration is even less than was to be expected for a linear relationship[54]. Sveshnikov's results, and also those of Kroh[105] indicating that the oxidation of lucigenin is of the first order, make the Gleu and Petsch and Karyakin–Erdey scheme the most probable. Tamamushi and Akiyama's hypothesis, according to which a quadratic dependence of reaction velocity on lucigenin concentration should be observed, obviously does not correspond to reality.

Lucigenin, like Luminol, is employed in analytical chemistry for the detection of copper(II), lead, and mercury(II)[104,106,107], as a chemiluminescent indicator[108,109], etc.

TABLE. Positions of chemiluminescence and photoluminescence maxima for lucigenin bromide (I), *NN'*-dimethylbiacridinylidene oxide (II), and *NN'*-dimethylbiacridinylidene (III).

Compound	Position of maximum		
	chemiluminescence	fluorescence	phosphorescence
I	480,515	480,515	480,515
II	550	505	548
III	525	515	523

VI. SYSTEMS SHOWING WEAK CHEMILUMINESCENCE

We have discussed above reactions which are accompanied by bright chemiluminescence. The high emission intensity in these reactions is due either to a high rate of occurrence of exothermic processes or to a high yield, i.e. the efficient conversion of chemical into light energy. These conditions are not satisfied in reactions occurring at moderate temperatures (low rates) and with the formation of products which are unable to luminesce efficiently (low yields). Such reactions will therefore be accompanied not by bright but by weak chemiluminescence, even if they include stages in which the energy evolved is equivalent to quanta of visible light. Nevertheless, it is clear that there is no fundamental, qualitative difference between systems having bright and those having weak chemiluminescence, and emission may be observed in many slow "ordinary" reactions provided that a sufficiently sensitive detector is available.

The first investigations of weak chemiluminescence were made before the Second World War by Audubert and his coworkers[110,111]. With the aid of Geiger–Müller counters they detected extremely weak ultraviolet emission in many reactions, such as the neutralisation of strong acids by strong alkalis, the hydration and dehydration of quinine sulphate, several oxidation–reduction reactions — the autoxidation of bisulphite, the oxidation of organic substances by permanganate, chromic acid, bromine, and iodine, the anodic oxidation of aluminium, magnesium, silicon, etc. The number of photons emitted from 1 cm^2 of surface in 1 s did not exceed 10^4 (in isolated cases 10^5). Hence the yield, i.e. the ratio of the number of photons emitted to the number of molecules which have reacted, was of the order of 10^{-14}–10^{-15}, which is extremely low. Only in the decomposition of azides was the emission sufficiently intense for its temperature coefficient and its spectrum to be determined.

A striking feature of Audubert's experiments was the huge size of the quanta emitted, the range 200–240 mμm corresponding to amounts of energy of 140–120 kcal. Nevertheless, the sum of the heat of reaction and the activation energy of the reactions investigated did not exceed 50–80 kcal. Audubert assumed that twin collisions could occur between energy-rich molecules of the products, but this hypothesis remained unproven.

At the end of the 1930s Audubert ceased to investigate chemiluminescence, and did not return to it again. One of his last papers on chemiluminescence finished with the words: "In the present state of the exceptionally unfavourable and technically difficult method it is not surprising that the number of results as yet obtained is small. But it is to be hoped that advances in the technique of photoelectric counters will make possible the widespread use of a method which has already yielded such interesting conclusions"[111]. In fact the application of highly sensitive light transducers — photomultipliers, photoresistors,

etc. — has enabled a weak emission to be detected in many chemical reactions, and its regularities to be investigated[112,113]. Luminescence in the visible region of the spectrum has been studied in — the thermal decomposition of peroxides, hydroperoxides, and azo-compounds in solution[112-115]; the thermal decomposition and oxidation in the gas phase of peroxides, hydroperoxides, alkyl iodides, alkyl nitrites, nitric acid, nitromethane[113,114], acetaldehyde[116], propionaldehyde and butyraldehyde[117], ethyl hyponitrite[118], n-hexane, and diethyl ether[117]; the electrolysis of ethanol, acetic acid, potassium acetate[113,114], sodium acetate, sodium propionate, sodium citrate, sodium tartrate, Grignard reagents, amino-acids, and several other organic substances[119]; the oxidation with oxygen of hydrocarbons and other organic compounds in solution[114,120-123]; the condensation of acid chlorides with amines and ketones, and polycondensation (production of nylon)[124,125]; the oxidative degradation of polypropylene and other polymers[126]; the oxidation of urea with hypohalites[127]; the oxidation of sodium sulphite in aqueous solution catalysed by metal salts[128]; and the oxidation of oxalyl chloride with hydrogen peroxide[129]

Thus chemiluminescence has been detected in a large number of reactions of the most varied classes and types. In view of these results, chemiluminescence must evidently be regarded as a general phenomenon, accompanying the occurrence of any reaction in which exothermic stages are involved.

1. Chemiluminescence in Induced Oxidations

Until recently no quantitative investigation had been made of chemiluminescence accompanying oxidation by molecular oxygen. In order to find a reaction in which excited species are formed, and compare the regularities in chemiluminescence with the kinetic regularities, a series of investigations[113,114,130,131] were based on induced oxidation as model reaction, the kinetics of which is well known[132-134]. The reaction scheme of an induced oxidation is

$$\begin{aligned}
&1)\ \text{chain initiation (appearance of radicals R) at rate } w_i\\
&2)\ R+O_2 \xrightarrow{k_2} RO_2 \\
&3)\ RO_2+RH \xrightarrow{k_3} ROOH+R \quad \Big\}\ \text{chain propagation,}\\
&4)\ R+R \rightarrow R-R\\
&5)\ R+RO_2 \rightarrow ROOR \\
&6)\ RO_2+RO_2 \rightarrow \text{inactive products} + O_2 \quad \Big\}\ \text{chain termination.}
\end{aligned} \tag{15}$$

where RH is the substance undergoing oxidation, ROOH the hydroperoxide, R the hydrocarbon radical, and RO_2 the peroxy-radical.

Examination of the energetics of reactions (1)–(6) in scheme (15) shows that only reactions (4)–(6) are sufficiently exothermic to excite luminescence in the visible region of the spectrum (the range 350–620 mμm corresponds to 80–45 kcal or 3.3–2.0 eV). At sufficiently high oxygen concentrations the radicals R are converted by reaction (2) into peroxy-radicals, and only RO_2 radicals recombine. Under these conditions the emission intensity I is proportional to the rate of recombination w_{rec}:

$$I = \eta_{ch} w_{rec} = \eta_{ch} k_6 (RO_2)^2, \tag{16}$$

where η_{ch} is the number of photons emitted in a single act of recombination.

Under steady-state conditions the rate of destruction of radicals is equal to their rate of formation w_i, which is proportional to the rate of decomposition of the initiator:

$$w_i = 2 f_{cell} k_0 c, \tag{17}$$

where c is the initiator concentration, k_0 its decomposition rate constant, and f_{cell} the probability of escape of primary radicals from the "cell", the factor 2 indicating that the decomposition of one molecule yields two radicals.

It follows from Eqns. (16) and (17) that

$$I = 2\eta_{ch} f_{cell} k_0 c.$$

If decomposition is slow, the intensity will not vary with time, and at a given temperature will be determined by the formula

$$I = 2\eta_{ch} f_{cell} c a_0 e^{-E/RT} = \text{const}\ e^{-E/RT}, \tag{18}$$

where a_0 is the preexponential factor and E the activation energy of decomposition.

Eqn. (18) indicates an Arrhenius temperature dependence for the intensity. This relationship is in fact well satisfied (Fig. 1), the activation energy determined experimentally from the chemiluminescence E_{ch} proving to be identical with E, the activation energy of decomposition of the corresponding substance measured by chemical methods[112-114,135].

If the rate of decomposition of the substance at the experimental temperature is considerable, the concentration will decrease according to the exponential law $c = c_0 e^{-k_0 t}$. The emission intensity should decay according to the same law:

$$I = I_0 e^{-k_0 t} \text{ or } \log I = \log I_0 - 0.43\, k_0 t.$$

This relationship has been observed, for example, in the decomposition of the intermediate product in the ozonisation of 2,7-dimethyloctane[136] and of ethylbenzene hydroperoxide[121], as well as of peroxides formed by the exposure of solutions of deoxyribonucleic acid to X-rays[137]. The decomposition rate constants determined from chemiluminescence data coincided with those obtained by chemical methods.

The kinetics of chemiluminescence may be different in complex reactions, since the rate of the exciting process may vary in a complicated fashion in the course of the chemical change. In the decomposition of the hydroperoxide of 1,1-diphenylethane in glacial acetic acid, for example, the emission intensity increases as a sigmoid curve, passes through a maximum, and then falls[115] (Fig. 2). An investigation comprising experiments with the addition of reactant and products while the reaction is

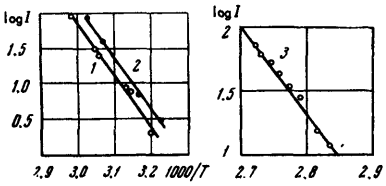


Fig. 1. Temperature dependence of the intensity of chemiluminescence in the oxidation of a series of hydrocarbons initiated by:
1) 2,7-dimethyloctane hydroperoxide; 2) tetralin hydroperoxide; 3) azoisobutyronitrile.

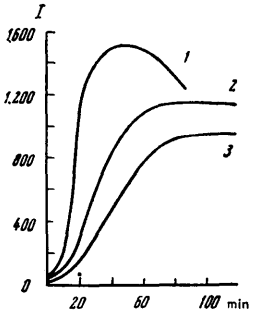


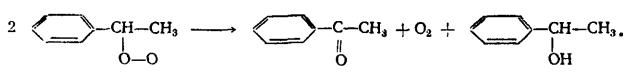
Fig. 2. Kinetic curves of chemiluminescence in the decomposition of 1,1-diphenylethane hydroperoxide in acetic acid at different temperatures and hydroperoxide concentrations: 1) 98.5° and 0.048 M; 2) 87° and 0.050 M; 3) 75.4° and 0.078 M.

progressing, dilution of the reaction mixture during the reaction, and studies of the effects of temperature and of the initial concentration of hydroperoxide has shown that the observed kinetics of chemiluminescence is governed by the formation of intermediate products. Breakdown of one of these products results in the formation of radicals, whose recombination excites the chemiluminescence[115]. Examples of the application of chemiluminescent methods to detect intermediate products in complicated reactions have been given also in papers[117,138] which are considered in other Sections of the present review.

It has been reported many times (see e.g. Ref. 139) that oxygen intensifies chemiluminescence, although it is an effective quencher of luminescence. This apparent contradiction has been eliminated by work[130] showing that oxygen exerts both stimulating and quenching effects. The stimulating action is observed at low oxygen concentrations, and is chemical in nature.

It follows from the reaction scheme (15) that, as the oxygen concentration increases, the concentration of RO_2 radicals also increases, as does the contribution of process (6). Hence the intensity changes, too, since the emission yield will depend on the structure of the reactant radicals and the products formed. The products of the recombination of RO_2 radicals are oxygen-containing compounds which luminesce in the visible or near ultraviolet region. Recombination of R radicals involves the formation of molecules which do not luminesce in the visible range. Therefore the conversion of chemical into excitation energy and the subsequent emission of light should occur far more efficiently in the former than in the latter case. This results in an intensification of the luminescence with increase in the concentration of oxygen. The stimulating effect of oxygen ceases when all the radicals have been converted into peroxy-radicals[120,130,138,140,141,159].

The disproportionation of, for example, peroxy-radicals of ethylbenzene involves the formation of 1-phenylethanol, acetophenone, and molecular oxygen[142]:



In order to identify the excited state, determinations were made of the quantum yield of the emission, the life of the excited state, and the luminescence spectra[140,143-145]. Examination of the results showed that the excited species responsible for the emission in the oxidation of ethylbenzene was acetophenone in its triplet state (one molecule of triplet acetophenone was formed in the reaction per 10^5–10^6 acts of recombination). Thus the chemiluminescence represents the radiative transition of acetophenone to the ground (singlet) state; the yield of this process is 1 photon per 10^3–10^4 excited molecules[140,145].

The views on the chemical mechanism of the intensification of luminescence by oxygen and on the excitation of chemiluminescence in the recombination of peroxy-radicals, formulated in Ref. 130, have subsequently been checked many times, and have been quantitatively confirmed by various methods.

2. Measurement of Rate of Oxidation

The marked difference in the emission yield of the recombination of $R^\cdot$ and of $RO_2^\cdot$ radicals has been used to measure the rate of induced oxidation[140,146]. In an experiment the solution was saturated with air or oxygen, and the reaction vessel closed. At this instant a gradual decrease in the concentration of dissolved oxygen in the system began. After a certain time t_f a fall in emission intensity was observed, caused by the complete exhaustion of O_2 and replacement of $RO_2^\cdot$ by $R^\cdot$ ("oxygen fall"). With many hydrocarbons the rate of oxidation is independent of the O_2 concentration right down to very low values of the latter (10^{-6}–10^{-5} M), which, incidentally, is responsible for the sharpness of the drop in emission. It may therefore be assumed that

$$w_{O_2} = \frac{d[O_2]}{dt} = \frac{[O_2]_0}{t_f}. \qquad (19)$$

and the rate of oxidation may be determined from t_f and $[O_2]_0$. The reliability of this method of measuring rate of oxidation has been tested and confirmed on the oxidation of several organic substances (ethylbenzene, cumene, toluene, decalin, cyclohexane, methyl oleate, n-decane, n-heptane, and ethyl methyl ketone) initiated by the thermal decomposition of azoisobutyronitrile and dicyclohexyl peroxodicarbonate[140]. According to scheme (15), the rate of oxidation is

$$w_{O_2} = \frac{k_3}{\sqrt{k_6}}[RH]\sqrt{w_i} + \frac{1}{2}w_i. \qquad (20)$$

The higher the concentration of hydrocarbon, the higher the rate of oxidation and the shorter the time t_f. This is clearly evident from Fig. 3. Eqns. (19) and (20) can be used to determine the concentration of dissolved oxygen $[O_2]$ and the ratio of the elementary rate constants $k_3/\sqrt{k_6}$, provided that the rate of initiation w_i is known. From the change in rate due to decomposition of the initiator and the known value of w_i we can determine the decomposition rate constant of the initiator k_0 and its efficiency f_{cell}[147] with the same accuracy as by the use of other methods for measuring the rate of oxidation.

Measurement of rate of oxidation at low hydrocarbon concentrations enables us to estimate the relative efficiencies of active initiator radicals in abstracting a hydrogen atom from the hydrocarbon[147]. It is also possible to obtain some qualitative information on the reaction. In a pure inert solvent, for example, $w_i = w_{O_2} = [O_2]_0/t_f$[146,147], whence it follows that molecular oxygen is not evolved in

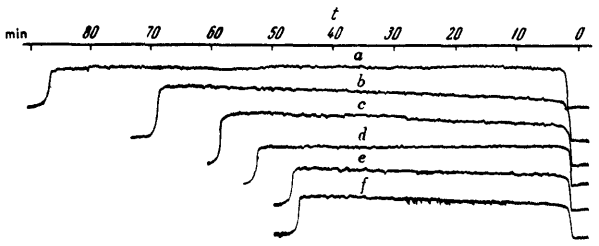


Fig. 3. "Oxygen falls" in chemiluminescence accompanying the oxidation of ethylbenzene in chlorobenzene as solvent, initiated by azoisobutyronitrile ($w_i = 1.9 \times 10^{-7}$ M s^{-1}), with different concentrations (M) of ethylbenzene:
a) 0.078; *b*) 0.234; *c*) 0.391; *d*) 0.548; *e*) 0.704; *f*) 0.781.[140,146]

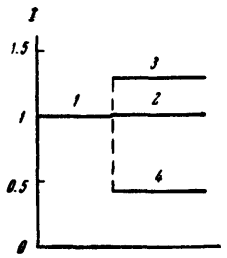


Fig. 5. Change in intensity of chemiluminescence accompanying decomposition of 1,1′-diphenylazoethane in chlorobenzene on addition of 2 vol.% of various hydrocarbons:
1) pure chlorobenzene; 2) addition of ethylbenzene; 3) diphenylmethane; 4) cyclohexene.

the recombination of active radicals of the initiator azoisobutyronitrile, whereas oxygen is always liberated in the recombination of hydrocarbon peroxy-radicals.

The kinetics of the consumption of oxygen and of the variation in emission intensity have been calculated on an M-20 electronic computer[140,148]. As can be seen from Fig. 4, the theoretical curve shows a considerable lack of symmetry: i.e. it has the same shape as the experimental curves. Comparison of theoretical and experimental curves enables the ratio $k_3/\sqrt{k_6}$ to be assessed as of the order of 10^3 litre$^{\frac{1}{2}}$ mole$^{-\frac{1}{2}}$ $s^{-\frac{1}{2}}$ for most of the hydrocarbons investigated.

The yield and intensity of chemiluminescence differ for the recombination of peroxy-radicals of different hydrocarbons[114,145,149,150]. The effect of radical composition on emission intensity is shown in Fig. 5, which illustrates the changes in intensity accompanying the decomposition of 1,1′-diphenylazoethane $C_6H_5.CH(CH_3).N:N.CH(CH_3).C_6H_5$ in chlorobenzene on addition of various hydrocarbons[150]. Decomposition of this azo-compound in the presence of molecular oxygen yields peroxy-radicals of ethylbenzene, the luminescence arising as a result of their recombination.

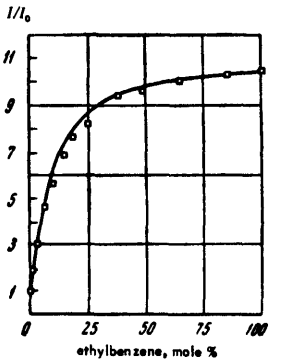


Fig. 6. Dependence of intensity of chemiluminescence on composition of mixture in the simultaneous oxidation of cumene and ethylbenzene initiated by the decomposition of azoisobutyronitrile at 60° and $w_i = 10^{-7}$ M s^{-1}. The points represent experimental values; the curve has been calculated.

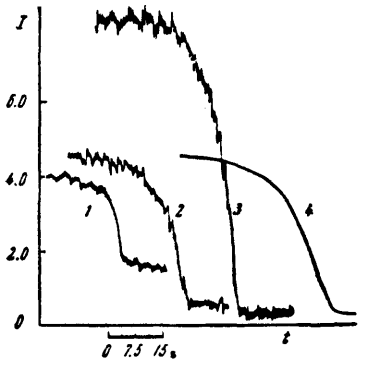


Fig. 4. Kinetic curves for the weakening of chemiluminescence, caused by replacement of peroxy-radicals by hydrocarbon radicals[140], in the oxidation, initiated by the thermal decomposition of azoisobutyronitrile (0.061 M) in benzene at 63°, of the hydrocarbons:
1) toluene; 2) ethylbenzene; 3) decalin; 4) theoretical curve.

Addition of 2% of ethylbenzene does not affect the emission intensity, since the concentration and composition of the radicals remain unchanged. Additions of other substances capable of reacting with peroxy-radicals of ethylbenzene change the intensity owing both to the appearance of a new species of radicals and new recombination reactions and to the decrease in the rate of recombination of the peroxy-radicals of ethylbenzene.

For the same reasons the intensity of luminescence in the simultaneous oxidation of two substances will depend on the composition of the mixture and the emission yields as well as on the kinetic parameters, the ratios of the rate constants for the elementary acts. Fig. 6 shows the dependence of emission intensity on the composition of a mixture of cumene and ethylbenzene undergoing oxidation. The full line represents the dependence calculated from the rate constants[151] and the measured quantum yields of chemiluminescence. The good agreement between calculated and experimental curves indicates that measurements of chemiluminescence can be used to determine the kinetic parameters of this complicated reaction[150].

3. Chemiluminescence in Inhibited Oxidations and the Activity of Inhibitors

The intensity of chemiluminescence in various oxidations with hydrogen peroxide and molecular oxygen has been observed to diminish on the addition of inhibitors of free-radical reactions[113,119,126,152-155]. In several cases the dependence of emission intensity on inhibitor concentration has been used to determine the concentration of the latter[122,156]. Until recently no quantitative study had been made of the relation between the activity of an inhibitor InH and its ability to diminish the intensity of luminescence. It became possible to solve this problem as a result of work establishing the mechanism of the excitation of chemiluminescence in oxidations with molecular oxygen[113,114,130]. In order to describe the process of inhibited oxidation, scheme (15) must be supplemented by the reactions[157,158]

$$\left.\begin{array}{ll} 7)\ \mathrm{InH}+\mathrm{RO}_2^{\bullet} \xrightarrow{k_7} & \mathrm{In}^{\bullet}+\text{ products},\\ 8)\ \mathrm{RO}_2^{\bullet}+\mathrm{In}^{\bullet} \xrightarrow{k_8} & \\ 9)\ \mathrm{In}^{\bullet}+\mathrm{In}^{\bullet} \xrightarrow{k_9} & \end{array}\right\}\ \text{stable products}.$$

The inhibitor radical In$^{\bullet}$ which is formed is usually inactive and incapable of participating in chain propagation. Additions of an inhibitor lower the concentration of peroxy-radicals and thus retard the oxidation. Since luminescence is associated with the recombination of $RO_2^{\bullet}$ radicals, the diminution in their concentration produced by the addition of inhibitors results in a weakening of chemiluminescence. After such addition new chemiluminescent reactions do not arise, since the In$^{\bullet}$ radicals formed are relatively inactive, and the heat evolved in reactions (8) and (9) is insufficient to excite luminescence in the visible region of the spectrum. This kinetic scheme, in which the power of inhibitors to weaken emission is linked with their activity towards $RO_2^{\bullet}$ radicals, has been put forward by one of the present authors[159].

As can be seen from the scheme (15), the rate of a chain oxidation is

$$w = k_3(\mathrm{RO}_2^{\bullet})(\mathrm{RH}). \qquad (21)$$

Therefore $w/w_0 = [RO_2^{\bullet}]/[RO_2^{\bullet}]_0$, where the subscript 0 denotes the absence of inhibitor. On the other hand,

$$\frac{I}{I_0}=\frac{[\mathrm{RO}_2^{\bullet}]^2}{[\mathrm{RO}_2]_0^2},\ \text{or}\ \sqrt{\frac{I}{I_0}}=\frac{[\mathrm{RO}_2]}{[\mathrm{RO}_2]_0^2}. \qquad (22)$$

Comparison of Eqn. (21) with (22) shows that

$$\frac{w}{w_0}=\sqrt{\frac{I}{I_0}}. \qquad (23)$$

The relationship (23) has been tested and confirmed experimentally[123,160]. Its applicability shows that the weakening of chemiluminescence is caused by the diminution in the concentration of peroxy-radicals§, and that the intensity of chemiluminescence is a measure of their relative concentration. Hence it at once follows that the relative activities of inhibitors can be characterised by their concentrations at which the emission intensity decreases, e.g. is halved[161] (which corresponds to a 30% decrease in the concentration of peroxy-radicals). The reciprocal of the inhibitor concentration is then taken as a measure of the activity. In this way a series of inhibitor activities — for phenols and amines[161] — has been obtained, characterising their reactivity towards peroxy-radicals.

New chemiluminescent methods have been proposed, based on the above kinetic scheme, for determining the activity of inhibitors. The dependence of emission intensity I on inhibitor concentration $[InH]_0$

$$\sqrt{\frac{I}{I_0}}=1+1.1\frac{k_7}{\sqrt{k_6}}\frac{[\mathrm{InH}]_0}{\sqrt{w_i}} \qquad (24)$$

has been obtained[162] from this scheme. The kinetic parameter $k_7/\sqrt{k_6 w_i}$ is then determined from the slope of the linear plot of $\sqrt{I/I_0}$ against $[InH]_0$.

The kinetic chemiluminescence curve, representing the increase in concentration of peroxy-radicals resulting from the gradual consumption of inhibitor, is S-shaped (Fig. 7), with a point of inflection at $I/I_0 = 0.55$.[162]

It has been shown[148] that in general the slope at the point of inflection on the kinetic curve of chemiluminescence $[d(I/I_0)/dt]_{max}$ should be proportional to the ratio $k_7\sqrt{w_i}/\sqrt{k_6}$ if the emission intensity varies as a result of the consumption of some substance by reaction with the radicals responsible for the luminescence. Proportionality is then maintained independently of what other elementary acts enter the reaction scheme. An actual calculation of the above scheme has enabled the proportionality coefficient to be evaluated[162]:

$$\left[\frac{d(I/I_0)}{dt}\right]_{\max}=0.22\frac{k_7}{\sqrt{k_6}}\sqrt{w_i}, \qquad (25)$$

and measurements of the maximum slope to be used to determine the parameter $k_7/\sqrt{w_i/k_6}$. By combining the relations (24) and (25) we can use chemiluminescence measurements to obtain values of the parameter $k_7/\sqrt{k_6}$, which characterises the relative activity of an inhibitor, and the rate of initiation $(w_i)_{calc}$.

Experiments on fifteen inhibitors (phenols and amines) have shown[163] satisfactory agreement with Eqn. (24). Application of Eqn. (25) revealed that the slope of the kinetic curves decreases with increase in the initial concentration of inhibitor $[InH]_0$. This was explained by a decrease in activity of the inhibitor as its concentration

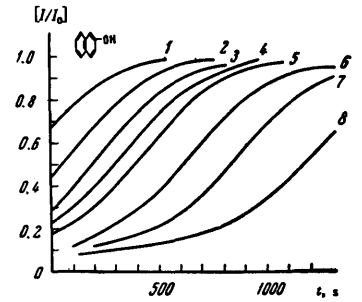


Fig. 7. Kinetic curves representing the variation in intensity of chemiluminescence accompanying the oxidation of ethylbenzene, initiated by the decomposition of azoisobutyronitrile at 60° and $w_i = 4.14 \times 10^{-7}$ M s^{-1}, in the presence of different initial concentrations (in 10^{-5} M) of 2-naphthol:
1) 0.69; 2) 1.38; 3) 2.07; 4) 2.76; 5) 3.45; 6) 5.17; 7) 6.9; 8) 9.5.

§ Many phenols are known as deactivators of excited states. Therefore the weakening of the luminescence might have been attributed *a priori* to physical quenching. The applicability of Eqn. (23) indicates that, under the experimental conditions, physical deactivation is negligible, if present at all, the chemical reaction of $RO_2^{\bullet}$ with InH being decisive.

increases. The same conclusion, on the concentration dependence of activity, was reached independently[164] from measurements of the activity of inhibitors from the rate of oxidation of styrene. The dependence of k_7 on $[InH]_0$ can be eliminated if data for a series of experiments with different values of $[InH]_0$ are used to extrapolate the maximum slope to $[InH]_0 \to 0$. Then simultaneous application of Eqns. (24) and (25) yields values of $k_7/\sqrt{k_6}$ and also of $(w_i)_{calc}$, the latter being practically identical with values of w_i specified in the experiment[163]. This identity of the values of w_i is a criterion of the correctness of the new chemiluminescent methods[163].

Experiments with a single inhibitor but in different oxidisable substances revealed a significant dependence of the ratio $k_7/\sqrt{k_6}$ on the nature of the oxidisable substance. The activity of $RO_2^\cdot$ varies comparatively little with the natue of the radical R,[151] so that values of k_7 should be similar for different $RO_2^\cdot$ radicals. At the same time, values of k_6 may differ by several orders of magnitude. If, therefore, values of $k_7/\sqrt{k_6}$ in two non-polar substances undergoing oxidation differ by a factor of more than 3–4, this is usually to be attributed to a difference in the values of k_6. On this reasoning it was concluded[163] that k_6 is considerably lower for 2,7-dimethyloctane than for ethylbenzene. This conclusion has been confirmed by direct experiments[165], in which concentrations of peroxy-radicals have been measured, by the electron spin resonance method, during the progress of liquid-phase oxidations.

Curves of the initial emission intensity and of the time of reaching the point of inflection, plotted as functions of the initial concentration of inhibitor from a series of kinetic chemiluminescence curves (Fig. 7), can be employed as calibration curves to determine inhibitor contents[122]. The sensitivity of the method depends on the value of w_i, and also on the activity of the inhibitor, reaching around 10^{-7} M. Since chemiluminescence is observed in the oxidation of various classes of substances — aldehydes, ketones, acids, alcohols, hydrocarbons, etc. — the proposed method can be used to determine inhibitor contents in practically any oxidisable substance[122].

The use of calibration curves enables us to determine with which radicals ($R^\cdot$ or $RO_2^\cdot$) a given inhibitor reacts. Experiments are carried out in which the inhibitor is subjected to the action of initiator radicals $R^\cdot$ in the absence of O_2 for a definite time. After this the kinetics of chemiluminescence, now in the presence of O_2, is recorded, and the change in concentration of inhibitor during reaction with $R^\cdot$ radicals is determined from the calibration curve. The experiments have shown, for example, that ionol does not react with $R^\cdot$ radicals[148].

4. Chemiluminescence in the Oxidation and Decomposition of Hydroperoxides Catalysed by Salts of Metals of Variable Valency

Chemiluminescence has been observed[115,121,166] in the oxidation of toluene, cumene, ethylbenzene, and diphenylmethane catalysed by the acetates or stearates of cobalt, manganese, and copper. The quantitative relationship between the kinetics of chemiluminescence and the kinetics of the reaction has been investigated in the oxidation of ethylbenzene in glacial acetic acid with cobalt acetate as catalyst[121,166]. Recently the kinetics of this reaction has been studied quantitatively by the usual methods[167,168]. Chemiluminescence was measured with the same specimen of catalyst under the same conditions. As a result, the kinetics of chemiluminescence could be directly compared with the reaction kinetics. The experiments showed that, in the course of the process, the emission intensity increases to a constant value independent of the catalyst concentration. Increasing the latter merely shortens the time needed to reach the steady state. Initial additions of a hydroperoxide eliminate the stage of increasing emission. The initial intensity of luminescence is proportional to the concentration of the additive. Soon after the start of the experiment the intensity reaches the same level as in the absence of an initial addition. Hence it follows that the observed kinetics of chemiluminescence is associated with the accumulation of hydroperoxide, and that the steady emission intensity corresponds to a steady state of oxidation, in which the rate of consumption of hydroperoxide is constant. The intensity of luminescence in the steady state is proportional to the rate of oxidation. As a result, intensity measurements can be used to obtain the fundamental kinetic parameters of the reaction — the dependence of rate of oxidation on the concentrations of hydrocarbon and of catalyst, and the activation energy of the reaction.

The observed regularities in chemiluminescence are explained quantitatively by the scheme representing the kinetics of the catalysed oxidation of ethylbenzene[167]. This scheme differs from that of oxidation initiated by thermal decomposition solely in the initiation reaction. In the present case formation of $R^\cdot$ or $RO_2^\cdot$ radicals at a rate w_i occurs on reaction of the hydroperoxide with the catalyst:

$$ROOH + nCo(AcO)_2 \xrightarrow{k_i} \text{free radicals.}$$

When the rates of formation and consumption of hydroperoxide become equal, the maximum reaction velocity w_{st} is reached, equal to the rate of initiation

$$w_{st} = k_i^2[RH]^2/k_6 = w_i.$$

The emission intensity is given by the equation

$$I_{st} = \eta_{ch}k_6[RO_2^\cdot]^2 = \eta_{ch}w_i = \eta_{ch}k_i^2[RH]^2/k_6,$$

i.e. $I_{st} \propto w_{st}$, in conformity with experiment[121].

In order to describe quantitatively the kinetics of chemiluminescence in the initial, non-stationary stage of the oxidation process, an investigation was made of the catalytic decomposition of ethylbenzene hydroperoxide by a chemiluminescent method and by analysis of the consumption of hydroperoxide[169]. Experiments were made with initial additions of hydroperoxide to a solution of the hydrocarbon in acetic acid. Fig. 8 shows that the emission intensity and the hydroperoxide concentration diminish exponentially during the course of the decomposition reactions. The straight lines have practically the same slope. This permits measurements of the kinetics of chemiluminescence to be used to determine k_{eff}, the effective decomposition rate constants for the hydroperoxide. Since the emission intensity is proportional to the hydroperoxide concentration, comparison of the initial intensity accompanying a definite initial addition of hydroperoxide with the steady-state intensity will yield the steady-state hydroperoxide concentration $[ROOH]_{st}$¶. It follows from the kinetic scheme that the rate of oxidation is

$$w_{O_2} = -\frac{d[O_2]}{dt} = k_{eff}[ROOH]_{st}.$$

¶ This method of determining the hydroperoxide concentration is of intrinsic interest, and can be employed to estimate traces of peroxy-compounds. Its limiting sensitivity of $5-10 \times 10^{-7}$ M considerably exceeds that of chemical methods of analysis[169].

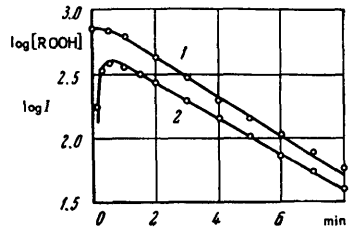


Fig. 8. Semilogarithmic anamorphoses of kinetic curves at 47° for 20% ethylbenzene (RH) in acetic acid containing 0.037 M ROOH and 0.032 M $Co(OAc)_2$: 1) decomposition of ethylbenzene hydroperoxide; 2) chemiluminescence.

To check the accuracy of chemiluminescent methods of determining k_{eff} and $[ROOH]_{st}$, a comparison was made between values of w_{O_2} and $k_{eff}[ROOH]_{st}$, which showed that the difference did not exceed 10–15%.[169]

Chemiluminescent methods have also enabled the mechanism of the catalysed decomposition of the hydroperoxide to be investigated[138]. The initial stage of the decomposition was observed to be accompanied by an increase in the emission intensity (Fig. 8), which was shown to be associated with the formation of an intermediate product, a cobalt(III) salt. This salt reacts with the hydroperoxide according to Eqn. (27):

$$\begin{aligned} &ROOH + Co(OAc)_2 \rightarrow RO_2^{\bullet} + Co(OH)(OAc)_2, \\ &Co(OH)(OAc)_2 + AcOH \rightarrow Co(OAc)_3 + H_2O, \end{aligned} \qquad (26)$$

$$ROOH + Co(OAc)_3 \rightarrow RO_2^{\bullet} + Co(OAc)_2 + AcOH, \qquad (27)$$

which results in an increase in the rate of decomposition and a corresponding intensification of the luminescence. From kinetic measurements on the growth and subsequent fall in the emission, the latter due to consumption of the hydroperoxide, the equilibrium concentration of the intermediate product could be determined kinetically. Calculations gave values of the order of 1% based on the concentration of the bivalent salt. Similar values for the concentration of the tervalent form of the catalyst were obtained in independent spectrophotometric experiments[170].

Chemiluminescent methods show that two different radicals are actually formed in the catalytic decomposition of the hydroperoxide[138]. When decomposition is carried out in the presence of oxygen, RO• radicals are converted into peroxy-radicals according to the scheme

$$\begin{aligned} &RO^{\bullet} + RH \rightarrow ROH + R^{\bullet}, \\ &R^{\bullet} + O_2 \rightarrow RO_2^{\bullet}. \end{aligned}$$

Half the peroxy-radicals are then formed from RO•, since in the steady state the reactions (26) and (27) occur at the same rate. If, when the steady state has been established, oxygen is removed from the system (by bubbling a pure inert gas through), the emission intensity drops sharply to a definite level lower than half the previous value. This result can be explained by the fact that, in the absence of oxygen, conversion of RO• into $RO_2^{\bullet}$ radicals is impossible, and that some of the $RO_2^{\bullet}$ radicals are used up by reaction with the hydrocarbon and hydrocarbon radicals. From the rate of decomposition of the hydroperoxide and the emission intensity before and after removal of oxygen, the rate of recombination of $RO_2^{\bullet}$ in the absence of oxygen can be determined. These results were used, with reactions (4) and (5) of scheme (15) taken into account, to calculate values of the parameter $k_3/\sqrt{k_6}$, which were close to those obtained by the usual kinetic methods[138].

5. Chemiluminescence in Low-Temperature Gas-Phase Oxidations

Little study has yet been made of chemiluminescence in the gas-phase oxidation of organic substances. Until recently, in effect, only visual observations had been made, in which the temperature range of the luminescence was determined. The emission intensity was found to increase with rise in temperature, and the range of chemiluminescence was displaced to lower temperatures with increase in concentration of the oxidisable substance[171,172]. Just as with liquid-phase reactions, the application of highly sensitive photometric instruments has made it possible to detect chemiluminescence in various reactions. In the case of reactions in which it had been known earlier, the limits to its observation could be greatly shifted towards lower temperatures.

A more detailed investigation has been made of the chemiluminescence accompanying the oxidation of acetaldehyde[116,117,173], the kinetics of which has been studied thoroughly[174,175]. Investigations were made at 100–200° and initial pressures of the reaction mixture varying from a few tenths to several hundred millimetres of mercury. Fig. 9 shows kinetic curves for the luminescence and the variation in pressure obtained in one of the experiments, as well as kinetic curves for the consumption of the reactants and the accumulation of the products of the reaction. The emission curve passes through two maxima, the first of which is sharp and the second very flat. The former

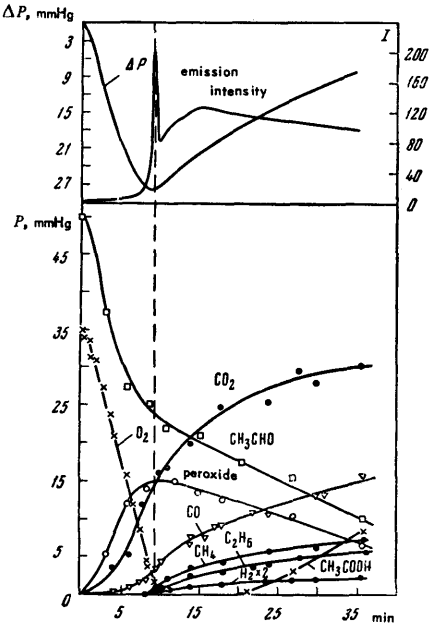


Fig. 9. Kinetic curves for intensity of chemiluminescence, pressure, consumption of reactants, and accumulation of products in the oxidation of acetaldehyde at 182°.

corresponds to a minimum on the pressure curve. This relationship is maintained however the experimental conditions are varied (by changing the temperature, pressure, and composition of the mixture, or adding a homogeneous catalyst). Oxygen quenches chemiluminescence, and the emission becomes stronger when its concentration is diminished[116]. At the instant at which the first maximum is reached, the process of oxidation with molecular oxygen terminates. This is evident both from the oxygen consumption curve and from the appearance of products (CH_4, C_2H_6, H_2) which could not be formed in the presence of oxygen. Thus the first luminescence maximum represents a change in the nature of the process, a transition from oxidation by molecular oxygen to oxidation by peroxy--compounds[174]. A similar sharp luminescence maximum was first observed in work on the oxidation of pentane[176], the author concluding from indirect arguments that this maximum was associated with the complete exhaustion of oxygen in the system.

Since the rate of consumption of oxygen is constant (Fig. 8), the time required to reach the first luminescence maximum can be conveniently used to determine the reaction velocity and its dependence on various parameters. It is obvious that

$$w_{O_2} = \frac{[O_2]_0}{t_{max}}.$$

With the rate of oxidation known, it is possible to obtain the principal kinetic characteristics — the activation energy, and the order with respect to the aldehyde, oxygen, and the total pressure — of the first stage of the reaction[117]. Kinetic parameters determined by the chemiluminescent method and from the fall in pressure are practically identical and agree with those determined by other methods[174,175].

It is possible to create artificially conditions under which the rate is constant, or the reaction will follow a known kinetic law. This can be achieved, for example, by carrying out a low-temperature initiated oxidation. In this case t_{max} can be used as a kinetic characteristic of different reactions, since an oxygen maximum is observed in the oxidation of many substances[117]. Determinations of the dependence of t_{max} on $[O_2]_0$ have enabled kinetic parameters to be evaluated[117] in the radical reaction of the oxidative decomposition of di-t-butyl peroxide and the chain oxidation of acetaldehyde:

for the reactions

$$CH_3^{\cdot} + O_2 \rightarrow CH_3OO^{\cdot} \ (k_2)$$

and

$$CH_3^{\cdot} + CH_3^{\cdot} \rightarrow C_2H_6 \ (k_4),$$

$k_2/\sqrt{k_4}$ = 123 litre$^{\frac{1}{2}}$ mole$^{-\frac{1}{2}}$ s$^{-\frac{1}{2}}$ at 105°;

for the reactions

$$CH_3CO^{\cdot} + O_2 \rightarrow CH_3CO_3^{\cdot} \ (k_2')$$

and

$$CH_3CO^{\cdot} + CH_3CO^{\cdot} \rightarrow (CH_3CO)_2 \ (k_4'),$$

$k_2'/\sqrt{k_4'}$ = 510 litre$^{\frac{1}{2}}$ mole$^{-\frac{1}{2}}$ s$^{-\frac{1}{2}}$ at 87°.

Determination of the chemiluminescence spectra has shown[173] that the luminescent species in the oxidation of acetaldehyde is the excited formaldehyde molecule. The presence of formaldehyde among the reaction products has been detected also by chemical analysis. From the dependence of the intensity of chemiluminescence on the concentration of oxygen, which obeys the Stern–Volmer equation, the lower limit to the life of excited formaldehyde has been found to be $\tau \geqslant 1.3$ μs.[177]

The problem of routes to the formation of excited formaldehyde has been discussed in the literature[178-182], mainly in connection with investigations on cold flames. The general view has now apparently become established that excitation occurs in reactions involving alkoxy-radicals[179-182]: e.g. in the case of methoxy-radicals

$$CH_3O^{\cdot} + CH_3O^{\cdot} \rightarrow CH_3OH + CH_2O + 76 \text{ kcal (Ref. 178)}, \quad (28)$$

$$CH_3O^{\cdot} + OH^{\cdot} \rightarrow H_2O + CH_2O + 98 \text{ kcal (Ref. 182)}, \quad (29)$$

$$CH_3O^{\cdot} + CH_3^{\cdot} \rightarrow CH_4 + CH_2O + 82 \text{ kcal}. \quad (30)$$

These heats of reaction are sufficient to excite formaldehyde (77 kcal)[183].

The formation of excited formaldehyde molecules is not a distinguishing feature of cold-flame oxidation, as has generally been assumed, for it occurs at considerably lower temperatures in slow oxidation processes. It has therefore proved possible to study the mechanism of the formation of excited formaldehyde molecules in model systems containing radicals of known composition[184]. The following sources of free radicals were used — (*a*) $CH_3^{\cdot}$ radicals from di-t-butyl peroxide $(CH_3)_3C.O.O.C(CH_3)_3$; (*b*) $CH_3O^{\cdot}$ radicals from[185] methyl nitrate CH_3ONO_2, methyl nitrite CH_3ONO, and dimethyl peroxide CH_3OOCH_3; and (*c*) $CH_3O^{\cdot}$ and $HO^{\cdot}$ from[185] methyl hydroperoxide CH_3OOH.

Luminescence was absent from the decomposition of methyl nitrate, methyl nitrite, dimethyl peroxide, and also a mixture of dimethyl and di-t-butyl peroxides, which enabled reactions (28) and (30) to be eliminated. The luminescence of formaldehyde was observed on decomposition of the hydroperoxide. The emission was sharply increased by additions of dimethyl peroxide, which itself decomposes without luminescence. The observed intensification of the emission is readily explained by an increase in the concentration of $CH_3O^{\cdot}$ radicals. Hence it follows that the excited formaldehyde is formed in reaction (29). An advantage of this process compared with (28) and (30) is its large heat of reaction.

Since there is no difficulty in introducing $CH_3O^{\cdot}$ radicals into a chemical system (by adding dimethyl peroxide, hyponitrites, etc.), the luminescence of formaldehyde may provide a convenient indicator for the detection of hydroxy--radicals. It is obvious that, conversely, hydroxyl may be an indicator of methoxyl (perhaps of alkoxyl) radicals[184].

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The results discussed in the present paper demonstrate the great possibilities and prospects for the application of chemiluminescent methods in the quantitative investigation of the kinetics and mechanism of various chemical processes. Recently the range of application of chemiluminescent methods of investigation has been greatly extended by the discovery of new chemiluminescent reactions. Chemiluminescent methods have been suggested for controlling technological chemical processes[186]. This in considerable measure stimulates interest both in the phenomenon itself and in the use of chemiluminescence to study the kinetics and the mechanism of chemical reactions.

NOTE ADDED IN PROOF

New results have recently been published on the luminescence of Luminol and lucigenin[187-189].

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THE PARTITION CHROMATOGRAPHY OF LIPIDS

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I. INTRODUCTION

Lipids of natural origin are usually mixtures of aliphatic compounds of different *classes*, characterised by a definite number of polar functional groups, COOH, OH, NH_2, etc. The structural differences between lipids within a given class are determined entirely by two parameters — the number of methylene groups and the number and position of double bonds. A set of lipids in which one of the parameters is constant while the other changes monotonically forms a *homologous series*. Each class may contain several such series. Their detailed analysis is of considerable theoretical and practical importance.

A mixture of lipids is separated into individual classes by adsorption chromatography; separation of the classes into homologous series and separation within the series generally does not take place in this case, since the differences in polarity among lipids within a class are small compared with the changes in polarity due to the functional groups. Even these relatively slight differences, however, are quite sufficient for the separation of lipids within classes and homologous series by the method of *partition chromatography*†.

Partition chromatography, discovered in 1941 by Martin and Synge [1], was applied in the field of lipids only in 1948, in work by Ramsey and Patterson [2] and Boldingh [3]. In the last 17 years, several hundred scientific papers and a large number of reviews [4-19] have been devoted to the partition chromatography of lipids.

The subject of the present review is the use of various types of partition chromatography in the analysis of natural

† This term, which is now firmly established, cannot be regarded as appropriate, since the mass is partitioned between solid, liquid, or gaseous phases in *any* chromatographic separation. Here and subsequently we shall have in mind *a system of two immiscible liquid phases*, one mobile and one stationary.