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U. D. C. 541.515 : 535.37

FREE RADICALS AND CHEMILUMINESCENCE

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I. INTRODUCTION

More than forty years ago, in the Laboratory of Electronic Chemistry of the Leningrad Physicotechnical Institute headed by Semenov, an investigation was begun of the mechanism and the kinetics of gas reactions, which subsequently resulted in a general theory of thermally explosive processes. New ideas on branching reactions, the possibility of isothermal chain explosions, on the effect of the dimensions of the reaction vessel and of additions of inert substances on the kinetics of chain reactions were developed on the basis of quantitative investigations of the oxidation of phosphorus vapour. It is interesting that the original aim of this work was not at all to investigate the kinetics of the process, but to study the effect of the oxygen pressure on the efficiency of the chemiluminescence accompanying oxidation. The impetus to make a kinetic study came from the discovery of peculiar and surprising critical phenomena. It was shown[1,2] that intense luminescence arises only within a definite range of oxygen pressures: at lower and higher pressures the reaction does not occur at all, and emission is absent. An experimental and theoretical analysis of this phenomenon by Semenov led to the formulation of the fundamental postulates of the theory of branched chain reactions. Thus it can be stated that a new stage in the development of kinetics and of several related fields of science began with investigations of chemiluminescence.

Although the oxidation of phosphorus was the first process explained in terms of the theory of branched chain reactions, the detailed mechanism of this process has hitherto been unknown, and the kinetic schemes which have been considered are hypothetical in character. Only the fact that the oxidation of phosphorus occurs by a radical-chain mechanism can be regarded as firmly established. It is therefore obvious that the chemiluminescence observed in this reaction is also due to the reactions of free radicals.

This conclusion, that chemiluminescence originates in the reactions of free radicals, applies not only to the oxidation of phosphorus. It applies generally to gas-phase reactions, and is firmly based on the pioneering quantitative investigations of chemiluminescence made by Polanyi, Kondrat'ev, Terenin, and their collaborators. Examination of the work of these and other authors on gas-phase systems shows that in all gas-phase chemical processes the occurrence of chemiluminescence is associated with the recombination (or disproportionation) of free radicals and atoms or with their addition to various species. The energy of these elementary acts is usually sufficient to produce electronically excited (or strongly vibrationally excited) species.

The principal laws of chemiluminescence were established on the basis of gas reactions. Its intensity was shown to be proportional to the rate of the elementary reaction in which excited species are formed. A quantitative study was made of the possible effect of secondary processes (quenching of excited states, transfer of energy) on the intensity of the emission. The investigations of chemiluminescence enabled quantitative information to be obtained on the relative and absolute concentrations of atoms and free radicals in flames and combustion products, on the rate constants of the reactions of these species, on the energy distribution of the products of elementary reactions, on the processes of energy exchange in collisions, on the bond energies in certain molecules, etc. The results of this work are quite well known, have been summarised in several reviews and monographs, and will not be considered in detail here. The purpose of the present review is to discuss the considerably less thoroughly studied question of the possibilities of using chemiluminescent methods in the quantitative investigation of the mechanism and the kinetics of radical and chain reactions occurring in the liquid phase. The possibilities of these methods have been demonstrated mainly in work on liquid-phase oxidation processes undertaken during recent years in the Institute of Chemical Physics of the USSR Academy of Sciences.

II. RELATION BETWEEN CHEMILUMINESCENCE AND MECHANISM OF THE OXIDATION OF ORGANIC SUBSTANCES BY MOLECULAR OXYGEN

It has recently been shown[3] that, in the liquid-phase oxidation of organic compounds by molecular oxygen, chemiluminescence arises in acts of disproportionation of peroxy-radicals. Therefore the intensity of emission in oxidation processes is characteristic not of the overall rate of the process but of the rate of interaction of peroxy-radicals, the intensity being proportional to the rate of this reaction.

In the simplest case, when a pure substance is undergoing oxidation with a fairly high oxygen concentration in the liquid phase, only one kind of radicals — peroxy-radicals of the oxidisable compound — is involved in the reaction. These radicals are formed either by reaction of the oxidisable substance with oxygen, as a result of thermal or catalytic dissociation of peroxy-compounds formed in the course of oxidation, or as a result of dissociation of specially added initiators. The radicals obtained take part in the chain reaction and are destroyed, thus exciting the luminescence.

In the steady state the rate of loss of radicals is equal to the rate of generation of chains. Hence in systems containing one species of free radicals, the intensity of the light is proportional to the rate of the process in which free radicals are formed, i.e. to the rate of initiation. The existence of this relationship enables chemiluminescence intensity measurements to be used as a rapid method for determining the kinetic characteristics of the initiation reaction (investigation of the mechanism of initiation, and determination of the activation energy, order, and rate constant of initiation, of number of radicals formed on the breakdown of one molecule of the initiator)[4-6].

Let us now examine a more complex system, containing two species — active and relatively inactive — of free radicals. Such a system can be obtained experimentally, for example, by adding an inhibitor to the oxidisable substance. In such a system one chemiluminescent reaction remains as before, since reactions of the inactive radicals (in this case inhibitor radicals) are insufficiently exothermic to excite chemiluminescence in the visible spectrum. Since some of the active peroxy-radicals are destroyed by interaction with the inhibitor, the rate of disproportionation of the peroxy-radicals does not equal their rate of formation, and the emission intensity I in such a system

measures not the rate of initiation but the concentration of peroxy-radicals RO_2, where $[RO_2] \propto \sqrt{I}$.

As the concentration of inhibitor interacting with the peroxy-radicals increases, the intensity of the emission diminishes. The concentration dependence of the emission intensity (with a constant rate of initiation) can be used[7-10] to measure the activities and concentrations of inhibitors, to determine the number of chains terminated by one molecule of inhibitor, to determine the rate of initiation, and also to investigate the mechanism of the inhibitor action.

If the reaction involves two species of active radicals, three chemiluminescent recombinations are possible in the system. Such a system can be obtained, for example, by adding a substance capable of reaction with the active radicals. One of the simplest systems containing two species of active radicals arises when small amounts of oxygen are introduced into a solution of an initiator in the oxidisable substance. Some of the alkyl radicals R present in the system are then converted by reaction with oxygen into RO_2. On the introduction of oxygen the intensity of the emission increases, since the oxygen-containing products of the recombination of the peroxy-radicals have emission bands in the visible part of the spectrum. Such bands are usually absent in the products of the recombination of R + R and R + RO_2 radicals. Therefore only one chemiluminescent reaction actually takes place in this system, and the emission intensity, as in the preceding case, measures the concentration of peroxy-radicals. The dependence of intensity on the concentration of dissolved oxygen in such a system can be used to estimate the relative reactivity of the alkyl radicals towards oxygen[11].

The quantum yield of chemiluminescence changes not only on passing from one type of radicals to another (e.g. from R to RO_2). It depends also on the structure of the radical R present in the free peroxy-radical. If peroxy--radicals of two kinds take part in the reaction (as e.g. in the co-oxidation of two compounds R^1H and R^2H), a change in the composition of the mixture is accompanied by a change in the relative concentrations of R^1O_2 and R^2O_2 radicals, and therefore the intensity of the emission depends on composition. When the chemiluminescence yields in simultaneous recombination reactions differ relatively little, the dependence of the intensity of emission on the concentration of one of the reactants is more complicated than in the preceding case. Under favourable conditions in such systems, however, it is possible to evaluate the kinetic parameters of the reaction from measurements of chemiluminescence[12].

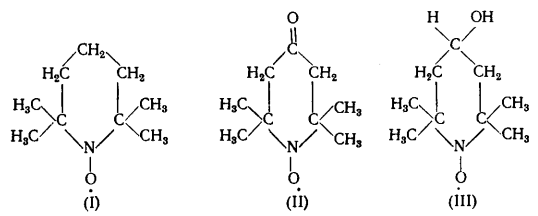
Thus quantitative studies of the laws of chemiluminescence in liquid-phase oxidations show that, in systems in which one chemiluminescent reaction occurs (or in systems in which the yield of chemiluminescence is much higher in one reaction than in the others), the emission intensity is a measure of the rate of recombination of free radicals. Therefore all factors which affect the concentration of radicals — temperature, reagent concentrations, additions of inhibitors, catalysts, etc. — influence the intensity of the luminescence. Furthermore, it is often possible from the emission intensity to follow the conversion of one kind of radicals into another. This opens up the possibility of determining from the emission intensity the relative concentration of free radicals and recording its variation both during the reaction and with change in the experimental conditions. In view of the great sensitivity of the chemiluminescent method, it is quite often the only direct method enabling changes in the concentration of free radicals to be recorded immediately.

III. USE OF CHEMILUMINESCENT METHODS TO INVESTIGATE THE MECHANISM OF THE ACTION OF ANTIOXIDANTS

In the present Section are discussed the results of several investigations in which the above ideas on the mechanism of chemiluminescence in inhibited oxidations have been used to elucidate the mechanism of the action of various inhibitors or antioxidants.

1. Mechanism of the Termination of Oxidation Chains by Stable Nitroxyl Radicals

Phenols and amines used as inhibitors form, on interaction with peroxy-radicals, unstable intermediate products, hydroperoxides, which readily break down to form free radicals, thus diminishing their effectiveness. Therefore great interest attaches to the search for inhibitors which terminate chains without forming branching agents. Among inhibitors of this type are the stable nitroxyl radicals



(I) (II) (III)

the mechanism of whose inhibiting action has been investigated[13].

Experiments were conducted with different concentrations of the nitroxyl radicals and different partial pressures of oxygen in the gaseous mixture bubbling through the oxidising ethylbenzene. During the experiments the concentrations of stable radicals were measured by the electron spin resonance method, and concentrations of peroxy--radicals by the chemiluminescent method. The experiments showed that, with sufficiently high oxygen concentrations, additions of stable radicals do not affect the intensity of the glow. Hence it follows that nitroxyl radicals R'NO· do not interact with the peroxy-radicals. They react vigorously, however, with alkyl radicals because, in the absence of oxygen, the nitroxyl radicals in concentrations exceeding 2×10^{-5} M are used up at the rate of initiation. Thus the inhibiting power of the nitroxyl radicals is determined by the relation between the rates of the two competing reactions

$$R + O_2 \xrightarrow{k_1} RO_2, \quad (1)$$

$$R + \dot{O}NR' \xrightarrow{k_2} \text{stable products.} \quad (2)$$

Fig. 1 shows how the emission intensity and the concentration of nitroxyl radicals (I) vary in the range of low oxygen concentrations when reactions (1) and (2) take place with comparable velocities. From these data the ratio of the kinetic constants $k_1/k_2 = 26 \pm 3$ for the nitroxyl radicals (I)–(III) was found. For the more stable alkyl radical of diphenylmethane this ratio is 1.4 ± 0.2, which can be explained by a lower value of k_1. Thus nitroxyl radicals can effectively suppress the oxidation chains of substances whose alkyl radicals are stabilised by conjugation and interact relatively slowly with oxygen, the effectiveness of the R'NO· radicals increasing as the oxygen concentration decreases.

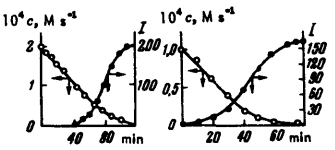


Fig. 1. Variation in concentration of nitroxyl radicals (I) and in intensity of chemiluminescence (in arbitrary units) at two initial concentrations of the nitroxyl radical (the nitrogen bubbling through ethylbenzene contains 9.3% of oxygen).

2. Interaction of the Hydroperoxide of Ethylbenzene with Benzenethiol in the Oxidation of Ethylbenzene

Available data [14-16] indicate that, in the oxidation of organic substances, compounds of the type of benzenethiol can react both with hydroperoxides and with peroxy-radicals. The occurrence of both reactions is readily detected from the kinetics of chemiluminescence [17]. The introduction of benzenethiol RSH into the oxidising ethylbenzene containing azoisobutyronitrile as initiator diminishes the emission intensity I. The dependence of I on [RSH] is of the same form as the corresponding relationship with other inhibitors, which do not react with the hydroperoxide, and it can be used to determine the rate constant for the reaction of benzenethiol with peroxy-radicals. Comparison with other inhibitors shows that benzenethiol reacts with peroxy-radicals just as effectively as does Ionol [4-methyl-2,6-di-t-butylphenol], which is frequently employed as an antioxidant.

Since benzenethiol acts as an inhibitor, it is gradually used up, and the emission intensity increases during the reaction. However, benzenethiol is consumed considerably more rapidly than is Ionol, which reacts solely with peroxy-radicals. This is seen formally from the fact that the mean number of chains terminated by one benzenethiol molecule is 0.3†, whereas Ionol terminates two chains. This difference can be explained by the additional benzenethiol required for reaction with the hydroperoxide. The latter reaction is detected from the chemiluminescence produced when benzenethiol is added to ethylbenzene containing hydroperoxide (~ 0.05 M). No emission is observed before the addition of benzenethiol, since the hydroperoxide dissociates too slowly under the experimental conditions. Additions of the inhibitor 1-naphthol weaken the resulting chemiluminescence. This implies that the hydroperoxide of ethylbenzene reacts with benzenethiol to form active radicals, which in ethylbenzene medium are converted into peroxy-radicals of ethylbenzene.

Thus an examination of the chemiluminescence shows that, in the initial stages of oxidation, when the hydroperoxide concentration is low, benzenethiol acts as an inhibitor. At later stages the additional reaction with hydroperoxide occurs.

† The number of chains terminated is determined from the kinetic chemiluminescence curves [10].

3. Synergic Action of Inhibitors in the Oxidation of Hydrocarbons

Fig. 2*A* shows kinetic chemiluminescence curves representing the consumption of two inhibitors and of a mixture thereof in the oxidation of ethylbenzene initiated by azoisobutyronitrile [18]. It is seen that 1-naphthol (curve *1*) is a stronger inhibitor than is Neozone D [*N*-phenyl-2-naphthylamine] (curve *2*). At time $t = 0$, 1-naphthol — a lower concentration of which was taken — diminishes the emission intensity just as strongly as does Neozone D. Consequently the two inhibitors are initially consumed at the same rate. Since the concentration of 1-naphthol is one-fifth, its relative rate of consumption is the higher. With a mixture of the inhibitors in the same concentrations (curve *3*) the 1-naphthol is used up first, and then the Neozone D. This is seen from the shape of the curves.

Quite different behaviour (Fig. 2*B*) is shown by another pair, Neozone D (curve *1*) and the phenolic inhibitor Azolactone‡ (curve *2*). It is seen from Fig. 2*B* that, of these two inhibitors, Neozone D is the more active. With the mixture (curve *3*), however, the weaker phenolic inhibitor is used up first, and then the more active inhibitor. This corresponds to the gently sloping initial portion of the chemiluminescence curve, and at the later stages to the considerably steeper section, identical in shape with the chemiluminescence curve in the presence of pure Neozone D. Nevertheless, the emission intensities at time $t = 0$ for both inhibitor mixtures (Figs. 2*A* and 2*B*) agree well with the calculated values obtained from the known rate constants for the interaction of each inhibitor separately with peroxy-radicals [19]. Hence it follows that the inhibitors do not interact at the instant of mixing.

Investigations [18-22] combining the chemiluminescent methods described above with the usual methods of analysing the consumption of inhibitors during oxidation have enabled the synergic effect (Fig. 2*B*) to be explained by means of the reactions

$$\mathrm{AmH} + \mathrm{RO_2^{\cdot}} \rightarrow \mathrm{Am^{\cdot}} + \mathrm{ROOH}, \quad (3)$$

$$\mathrm{Am^{\cdot}} + \mathrm{PhOH} \rightarrow \mathrm{AmH} + \mathrm{PhO^{\cdot}}, \quad (4)$$

where AmH and Am· are respectively the amine and the free radical, and PhOH and PhO· the phenolic inhibitor and

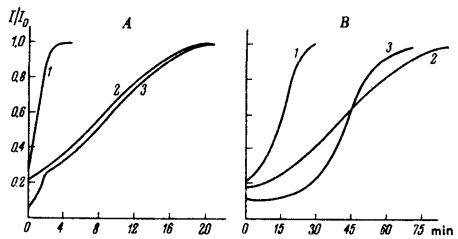


Fig. 2. Kinetic curves of chemiluminescence in the oxidation of ethylbenzene inhibited by additions of:
A): 1) 1-naphthol (0.22×10^{-5} M); 2) Neozone D (10^{-5} M); 3) a mixture of these inhibitors in the same concentrations;
B): 1) Neozone D (1.5×10^{-5} M); 2) the phenolic inhibitor Azolactone (4×10^{-5} M); 3) a mixture of these two inhibitors in the same concentrations.

‡ 4-(4-Hydroxy-3,5-di-t-butylbenzylidene)-2-phenyloxazolone.

the resulting free radical. It follows from this scheme that the more active inhibitor — the amine — interacts with the peroxy-radicals, but is regenerated by reaction (4). As a result, the amine begins to be used up only after the weak, phenolic inhibitor has been consumed.

4. Mechanism of the Inhibiting Action of Phosphorous Esters

In order to elucidate the mechanism of the inhibiting action of phosphites, the kinetics of chemiluminescence has been investigated[23] in the oxidation of ethylbenzene, initiated by azoisobutyronitrile, in the presence of phosphites having various structures and of substances forming part of phosphite molecules. It has been shown, by the methods already described above, based on the weakening of chemiluminescence and on its kinetics, characterising the consumption of inhibitor, that only phosphites containing phenolic substituents possess high activity towards peroxy-radicals. Alkyl-substituted phosphites and phosphates, as well as phosphorous acid, hardly react at all with peroxy-radicals.

An interesting feature of the kinetic curves of chemiluminescence in the presence of phosphites containing phenolic substituents is that these compounds lower the emission intensity very little, and in this respect behave as weak inhibitors, while being at the same time very rapidly used up, like strong inhibitors, their rate of consumption exceeding by factors of 10–100 the rate of formation of radicals by dissociation of the initiator. If these compounds are stored not in a vacuum but in contact with the atmosphere, increase in the period of storage results in a gradual change in the character of the kinetic curves: the phosphites weaken the emission to an increasing extent, and their rate of consumption constantly decreases, approaching the rate of initiation. Hence it follows that the inhibiting power is possessed not by the phosphites themselves but by the phenols formed by hydrolysis of the former on storage. If a few per cent of a strong inhibitor is formed on hydrolysis, little weakening of the luminescence results, since the concentration of the added inhibitor is less than that of the phosphite by factors of several tens, and the calculated rates of consumption are far too high, since the calculation is based on the concentration of added phosphite.

This hypothetical mechanism is supported by an analysis of the emission curves in the presence of sufficiently high phosphite concentrations. Fig. 3 shows as example the emission curve for *o*-phenylene tri-t-butylphenyl phosphite. The curve contains two clearly marked sections *ab* and *bc*. The maximum slopes of these sections α agree precisely with the values α_1 for catechol (section *ab*) and α_2 for tri-t-butylphenol (*bc*), as shown by the broken straight lines. Thus the inhibiting action of phosphite in oxidation reactions is due to the reactions of their hydrolysis products.

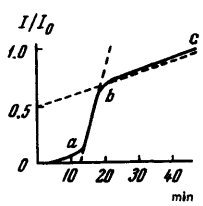


Fig. 3. Variation in relative intensity of chemiluminescence in the oxidation of ethylbenzene inhibited with added *o*-phenylene tri-t-butylphenyl phosphite.

IV. CHEMILUMINESCENT METHODS FOR MEASURING THE RATE CONSTANTS OF THE REACTIONS OF FREE RADICALS

Most methods for determining the rate constants for reactions of free radicals are based on measurements of non-stationary kinetics. Great difficulties are involved in determining kinetic constants by the direct measurement of steady-state concentrations of radicals. Slow chemical processes usually occur with low stationary radical concentrations, and only in rare cases is it possible to find a sufficiently sensitive method of measurement. The determination of the rate constants for reactions of free radicals is usually a complicated and laborious matter. The task is considerably simplified in several cases by the chemiluminescent methods which have appeared recently.

1. Chemiluminescent Method of the Photochemical Aftereffect

This method is based on measuring the kinetics of chemiluminescence in oxidation occurring under non-stationary conditions as a result of an abrupt change in the rate of initiation[24]. The time variation in the concentration of radicals under non-stationary conditions is described by the equation

$$\frac{d[RO_2]}{dt} = w_i - k_6[RO_2]^2, \qquad (5)$$

where w_i is the rate of initiation and k_6 the rate constant for recombination of the radicals. The form of solution of Eqn. (5) is determined by the initial conditions. If the photochemical reaction is conducted with a constant intensity of the exciting light, i.e. with constant w_i, a steady-state concentration of radicals

$$[RO_2]_{st} = \sqrt{\frac{w_i}{k_6}}, \qquad (6)$$

is established in the system.

After the light has been switched off, $w_i = 0$, and the concentration of radicals will fall as a result of their recombination:

$$-\frac{d[RO_2]}{dt} = k_6[RO_2]^2. \qquad (7)$$

The solution of Eqn. (7) is of the form

$$\frac{[RO_2]_{st}}{[RO_2]} - 1 = k_6[RO_2]_{st}t. \qquad (8)$$

Changing from radical concentrations to intensities, and making use of Eqn. (6), we obtain the expression

$$\sqrt{\frac{I_{st}}{I}} - 1 = \sqrt{k_5 w_i}\, t. \qquad (9)$$

which enables k_6 to be evaluated from the kinetics of the decay of chemiluminescence. Experimental determination of w_i in Eqn. (9) presents no difficulty, and can be effected in various ways.

The mean life of the radicals is

$$\tau = \frac{1}{\sqrt{w_i k_6}}. \qquad (10)$$

The recombination rate constants of peroxy-radicals usually lie within the range 10^4–10^8 litres mole^{-1} s^{-1}. The high sensitivity of the chemiluminescent method enables experiments to be conducted at w_i of the order of 10^{-10} M$\times$ $\times$ s^{-1}. Under these conditions 10 s $\leq \tau \leq$ 1000 s, and the experimental measurement of the kinetics of chemiluminescence can be made with standard equipment using ordinary EPP-09 pen-recorders.

2. Chemiluminescent Method of the Oxygen Aftereffect

The oxygen aftereffect method[24-26], like that of the photochemical aftereffect, is used to determine recombination rate constants of the radicals from the kinetics of the establishment of a steady state recorded from the chemiluminescence. The difference consists in the method used to obtain a non-stationary concentration of radicals. In the oxygen aftereffect method, a non-stationary concentration of peroxy-radicals is produced by rapidly feeding oxygen to a system comprising a compound RH capable of oxidation and an initiator Y.

Before oxygen is admitted, the reactions

$$\mathrm{Y} \rightarrow \mathrm{R'} + \mathrm{R'} + \text{products}, \quad (\text{rate of initiation } w_i)$$

$$\mathrm{R'} + \mathrm{RH} \rightarrow \mathrm{R'H} + \mathrm{R},$$

$$\mathrm{R} + \mathrm{R} \rightarrow \mathrm{R_2},$$

take place in such a system, and the steady-state concentration of R radicals is

$$[\mathrm{R}]_{st} = \sqrt{\frac{w_i}{k_4}}.$$

At the instant at which oxygen enters, the R radicals are converted very rapidly into RO_2 radicals by the reaction

$$\mathrm{R} + \mathrm{O_2} \rightarrow \mathrm{RO_2}, \qquad (11)$$

the rate constant of which is so large that the change occurs in a very short time, and it can be assumed that the concentration of peroxy-radicals at the instant of entry of oxygen is $[RO_2]_0 = [R]_{st}$. Since the recombination rate constant of peroxy-radicals k_6 is in general different from the rate constant k_4, the initial concentration of the radicals $[RO_2]_0$ will be non-stationary. After the admission of oxygen and the conversion of R into RO_2 radicals, therefore, the concentration of the latter will begin to change, tending to the stationary value

$$[\mathrm{RO_2}]_{st} = \sqrt{\frac{w_i}{k_6}}.$$

The kinetics of the variation in concentration of peroxy--radicals, and hence in the emission intensity, are described by the equations

$$\ln \frac{[\mathrm{RO_2}]_{st} + [\mathrm{RO_2}]}{[\mathrm{RO_2}]_{st} - [\mathrm{RO_2}]} \frac{[\mathrm{RO_2}]_{st} - [\mathrm{RO_2}]_0}{[\mathrm{RO_2}]_{st} + [\mathrm{RO_2}]_0} = 2\sqrt{w_i k_6}\, t, \qquad (12)$$

$$\ln \frac{\sqrt{I_{st}} + \sqrt{I}}{\sqrt{I_{st}} - \sqrt{I}} \frac{\sqrt{I_{st}} - \sqrt{I_0}}{\sqrt{I_{st}} + \sqrt{I_0}} = 2\sqrt{w_i k_6}\, t, \qquad (13)$$

obtained by solving Eqn. (5) with the condition $[RO_2] = [RO_2]_0$ at $t = 0$. The use of Eqn. (13) enables k_6 to be evaluated.

Since

$$k_4[\mathrm{R}]^2_{st} = k_4[\mathrm{RO_2}]^2_0 = k_6[\mathrm{RO_2}]^2_{st} = w_i,$$

the value of k_6 thus obtained can be used to determine k_4:

$$k_4 = k_6 \frac{[\mathrm{RO_2}]^2_{st}}{[\mathrm{RO_2}]^2_0}$$

or

$$k_4 = k_6 \frac{I_{st}}{I_0}. \qquad (14)$$

Thus the oxygen aftereffect method enables not only the recombination rate constant of peroxy-radicals k_6 (a process accompanied by luminescence) but also the rate constant for R radicals (recombination of which involves practically no emission) to be determined from a single experiment.

Fig. 4 shows possible kinetic curves for chemiluminescence with various relationships between the constants k_4 and k_6. Only when $k_4 = k_6$ (Fig. 4, curve *3*) does the oxygen aftereffect method become inapplicable.

The oxygen aftereffect has been measured[24] in the oxidation of cumene and of ethylbenzene. The measurements show that for cumene $k_4 \gg k_6$, as can be seen from the absence of an initial jump in intensity in the kinetics of the chemiluminescence (Fig. 5). In this case it can be assumed that $[RO_2]_0 = 0$, and the kinetics can be described by Eqn. (13) in the form

$$\ln \frac{\sqrt{I_{st}} + \sqrt{I}}{\sqrt{I_{st}} - \sqrt{I}} = 2\sqrt{k_6 w_i}\, t. \qquad (15)$$

This equation reproduces the experimental relationship well (Fig. 5). The value obtained for k_6 agrees well with the value determined by the classical method of intermittent illumination[27].

Kinetic curves of the type of curve *2* in Fig. 4 were obtained for ethylbenzene (Fig. 5), and from them recombination rate constants of 4×10^7 (k_6) and 2×10^8 litres mole$^{-1}\times$ $\times$ s^{-1} were obtained for peroxy-radicals and hydrocarbon radicals respectively.

The oxygen aftereffect method has been employed[28] to investigate the effect of the solvent — glacial acetic acid — on the recombination rate constant k_6 of peroxy-radicals from cumene. It was found that k_6 increases with increase in the acid concentration, being approximately doubled on passing from pure cumene to a 30% solution of cumene in the acid,

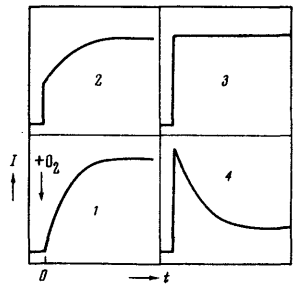


Fig. 4. Diagrammatic kinetic curves of chemiluminescence:
1) $k_4 \gg k_6$; 2) $k_4 > k_6$; 3) $k_4 = k_6$; 4) $k_4 < k_6$.

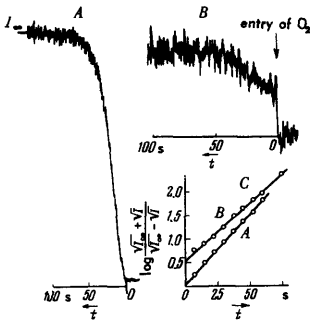


Fig. 5. Kinetics of chemiluminescence after rapid saturation with oxygen:
A) cumene, with dicyclohexyl peroxodicarbonate as initiator at 40° with $w_i = 1.49 \times \times 10^{-8}$ M s^{-1}; *B*) ethylbenzene with azoethylbenzene as initiator at 36° with $w_i = 1.75 \times \times 10^{-8}$ M s^{-1}; *C*) anamorphoses of curves *A* and *B*.

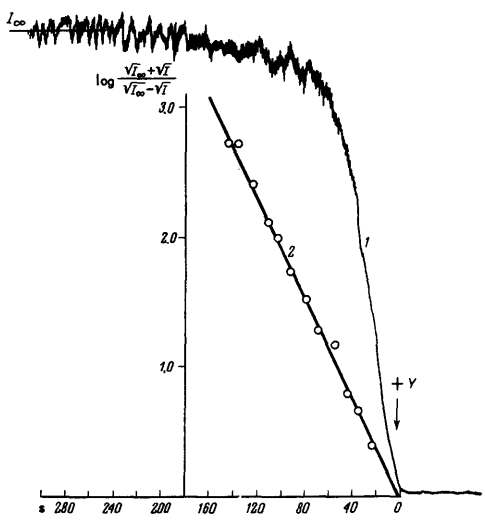


Fig. 6. Kinetics of chemiluminescence *I* after introduction of initiator Y (at instant indicated by arrow) into a solution of butan-2-one in benzene (1 : 4) with $w_i = 3.8 \times 10^{-8}$ M s^{-1} at 60°:
1) kinetic curve; 2) semi-logarithmic anamorphosis of curve 1.

while the rate constant of chain propagation remains practically unchanged. As a result of the increase in k_6, the rate of oxidation of cumene in the 30% solution falls by one-third (with the effect of dilution taken into account).

3. Chemiluminescent Method of Rapid Heating

Apart from the methods already described for producing non-stationary conditions in order to determine the rate constants of radical reactions from the kinetics of chemiluminescence, we can use rapid heating, addition of some reagent (initiator, oxidisable substance, inhibitor, etc.), cessation or change in intensity of initiation accomplished by means of ultrasonic vibrations, penetrating radiation, an electrode reaction, etc. Only some of these methods have hitherto been used in measuring rate constants. Thus the heating method has been used[29-31] in estimating the recombination rate constant for radicals of the initiator azoisobutyronitrile. The method involves adding a small volume (~ 0.1–0.01 ml) of the initiator to a heated inert solvent — chlorobenzene (containing an activator — a substance which intensifies the emission — and oxygen) — and recording the kinetic chemiluminescence curve, which reflects the kinetics of the accumulation of initiator radicals. At the instant of addition of the initiator $[RO_2]_0 = 0$, $I = 0$, and the kinetics of chemiluminescence is described by Eqn. (15).

According to these estimates $3 \times 10^7 < k_6 < 9 \times 10^7$ litres $\times$ $\times$ mole^{-1} s^{-1};[29] a value of $(1.6 \pm 0.8) \times 10^8$ litres mole^{-1} s^{-1} has been given in Ref. 31.

The heating method has been used[32] to investigate the effect of the medium on the recombination rate constant of the peroxy-radicals of butan-2-one. The difference from the work just mentioned consisted in adding a small volume of initiator solution not to a heated inert solvent but to the oxidisable substance (butan-2-one) or to a mixture of the latter and some solvent (benzene, water, nitrobenzene). The kinetics of chemiluminescence in this system is also described by Eqn. (15), which, as can be seen from Fig. 6, is well satisfied.

It was shown[32] that additions of benzene and water produce a decrease in the values of k_6, whereas additions of nitrobenzene produce an increase. The effects are quite marked: addition of 20 mole % of benzene more than halves k_6, and of water diminishes it almost to one-quarter whereas this addition of nitrobenzene produces a sevenfold increase in k_6.

It may be remarked that Refs. 28 and 32 report the first investigations of the effect of a solvent on the rate constants of the elementary reactions of free radicals in oxidation processes. Such studies have not previously been made, since the measurement even of one value of a constant was extremely time-consuming.

V. CHEMILUMINESCENCE OF IRRADIATED PROTEINS, NUCLEIC ACIDS, AND SYNTHETIC POLYMERS

Research papers have recently appeared on the chemiluminescence of irradiated proteins, nucleic acids, and synthetic polymers, which have established a link between free-radical processes and chemiluminescence. Chemiluminescent methods have been employed in this work to identify free radicals, determine the kinetics of radical destruction, reveal the reactions leading to the formation of free radicals, and assess the protective effect against radiation of compounds of various classes.

Chemiluminescence has been detected[33-35] in dry irradiated synthetic polymers and biopolymers, such as poly(methyl methacrylate), polystyrene, bovine serum albumin, human serum albumin, egg albumin, casein, etc. Comparison of the curves for the decay in chemiluminescence and for the fall in concentration of free radicals after irradiation (radical concentrations measured by the electron spin resonance method) showed that the chemiluminescence curves represent quantitatively the fall in radical

concentration. If the emission and radical-concentration curves are superposed at one point by changing the scale of the vertical axis, the curves coincide completely. This permits the chemiluminescent method to be used to investigate the kinetics of radical destruction at small radiation doses, when the sensitivity of the electron spin resonance spectrometer is inadequate.

Similar relationships have been obtained in studying the flash of chemiluminescence accompanying the dissolution of irradiated proteins and polymers[35]. Fig. 7 shows the kinetic curves for emission (full line) and radical concentration (points) in the dissolution of irradiated poly(methyl methacrylate) in dichloroethane. It is seen from Fig. 7 that in this case, too, the time variation of the emission reproduces the kinetics of the loss of radicals.

The luminescence becomes weaker or completely disappears when oxygen is removed. Addition to the solution of inhibitors for free-radical processes (e.g. Ionol) results in a diminished intensity of emission.

It was shown in the above papers that luminescence was associated with the recombination of peroxy-radicals. The coincidence of the kinetic curves for emission and loss of radicals was explained by limitation of the kinetics by processes of dissolution and diffusion of oxygen in the solvent. In view of the complexity of the systems, the experimental results do not yet provide, in the absence of many postulates, quantitative information on the elementary processes of the addition of oxygen or on the recombination rate constants of the radicals.

The investigation of the reactions of free radicals in solution is of special interest to radiation biology. Chemiluminescent methods can also be used in this work. Employment of a highly sensitive flow-type apparatus[36] has enabled a prolonged afterglow to be recorded in aqueous solutions of certain proteins and polymers — serum albumin, haemoglobin, trypsin, poly(ethylene oxide), polyvinylpyrrolidone, etc. — which have been irradiated with small doses of ultraviolet radiation and X-rays[37,38]. The investigation led to the conclusion that the afterglow represented chemiluminescence accompanying the recombination of peroxy-radicals[38].

Investigation of the effect of various substances on the kinetics of the afterglow has shown[39,40] that the rate of extinction of the light is most strongly increased by substances which possess a protective action against radiation (those containing sulphur, phenols). These substances

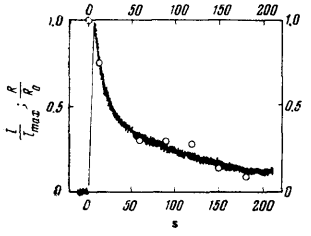


Fig. 7. Kinetics of the variation in the relative intensity of chemiluminescence (full curve) and kinetics of variation in relative concentration of radicals (points on curve) in the dissolution of irradiated poly(methyl methacrylate) in 1,2-dichloroethane.

influence the kinetics still more strongly if they are introduced into the system before exposure. Substances with feebly developed radiation-protective properties, however, exert little influence on the kinetics of the afterglow. Further investigation of the mechanism of the long-lived afterglow will probably help to elucidate several aspects of the primary action of radiation. Determination of the kinetics of the afterglow may also prove useful for a preliminary selection of radiation-protective substances.

A study has been made[41,42] of the afterglow in aqueous solutions of deoxyribonucleic acids (DNA) which have been irradiated at room temperature. Chemiluminescence was observed when the solutions were heated above 40°. The luminescence was shown to be associated with the breakdown of unstable peroxy-compounds of the DNA, formed during irradiation in the presence of oxygen. The kinetics of the decay of the emission, representing the rate of decomposition of the initiator, was used to evaluate the decomposition rate constants of the peroxy-compounds and the activation energy (13 kcal mole^{-1}). This value is identical with the activation energy for breakdown of the least stable DNA hydroperoxide and cytosine hydroperoxide[42]. The initial emission intensity is proportional to the concentration of peroxy-compounds of the DNA, and this relationship can be used to determine the content of peroxy-compounds in the irradiated solutions. Chemiluminescence in these systems is obviously associated with the reactions of free radicals, as is indicated by the weakening of the glow produced by antioxidants. Those inhibitors (e.g. propyl gallate) which considerably diminish the postradiation fall in viscosity of DNA solutions are most effective in diminishing the intensity of the chemiluminescence of DNA. When inhibitors which have a feeble effect on the postradiation fall in viscosity are added after irradiation, the emission intensity also changes insignificantly. These results again show the possibility of employing chemiluminescent methods to assess the radiation-protective effects of different compounds.

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FORMATION OF RADICALS IN REACTIONS BETWEEN VALENCY-SATURATED MOLECULES

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I. INTRODUCTION

It is well known that radical formation often occurs by unimolecular decomposition of various compounds with fission of the weakest bond in the molecule, e.g. by decomposition of peroxides at the O–O bond, of azo compounds at the C–N bond, of organometallic compounds at the metal–carbon bond, etc.

In recent years, evidence has accumulated in favour of the possibility of free-radical formation by a bimolecular reaction between valency-saturated molecules:

$$R'X + YR'' \rightarrow R'\cdot + XY + R''\cdot. \qquad (1)$$

In 1954, Semenov[1] published the first theoretical discussion, in a general form, of the kinetic features of reactions of this type, and arrived at the seemingly paradoxical conclusion that their activation-energy barrier should be relatively small.

This conclusion was reached on applying the principle of detailed equilibrium to certain reactions of atoms and radicals. Thus, we know[2] that the disproportionation of free ethyl radicals occurs with a very low activation energy. Hence it is a thermodynamic necessity that the reverse reaction (formation of two ethyl radicals from a molecule of ethylene and one of ethane) should also be attended by a negligible activation barrier[3], and that its activation energy should be fully accounted for by the endothermicity of the process (~ 60 kcal mole^{-1}).