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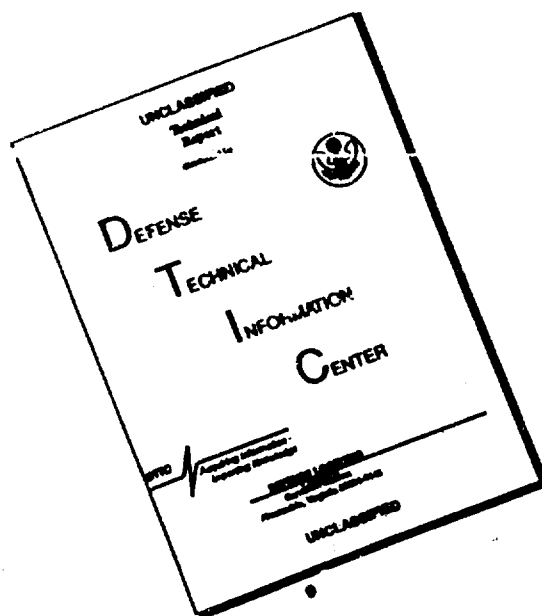
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THE MECHANISM OF CHEMILUMINESCENCE IN OXIDATIVE REACTIONS
IN SOLUTIONS

Trudy Moskovskogo obshchestva
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The main problem in investigating the mechanism of chemiluminescence is the identification of the excited state. In so doing, two groups of problems arise. Firstly, it is necessary to point out in what acts of the reaction the formation of an excited particle occurs and what factors determine the effectiveness of excitation. Secondly, it is necessary to point out in what manner and how effectively the energy of excitation is converted into radiation. The first group of problems is of a "chemical" character and is determined by the specific agent of excitation occurring at the expense of the energy of the chemical reaction. The second group is of a "physical" character: the fate of the excited molecules does not depend on the excitation agent but is determined by the same physical processes (radiating and radiationless conversions, energy transfer, quenching, etc.).

Thus, chemiluminescence is distinctly divided into two stages - - excitation and radiation. Each stage can be characterized by its yield or output: η_p^{exc} is the ratio of the number of excited molecules (P^*) of the product to the total number of formed molecules; η_p is the ratio of the number of molecules P^* given off as energy in the form of light quanta to their total number. The number of product molecules formed in a unit of time is the speed of the reaction, w . The number of light quanta emitted in a unit of time is the intensity, I . Consequently:

$$I = \eta_p \eta_p^{exc} w = \frac{ch}{\lambda} w. \quad (1)$$

The total yield of chemiluminescence (η_{chl}) in radical reactions in a solution is very low and does not exceed 10^{-6} quanta per one formed

molecule (Vasil'yev, Karpukhin, Shlyapintokh, 1959; Vasil'yev, Vichutinskiy, et al., 1961). Therefore, the luminescence is of slight intensity and can be detected by the use of highly sensitive photometric devices (Vasil'yev, Karpukhin, Shlyapintokh, 1961).

Despite the fact that the processes determining the stages of excitation and radiation are by nature different, they proceed simultaneously, and the solution of the basic problem concerning the nature of the excited state necessitates the consideration of both aspects of the phenomenon.

These considerations underlie our work, the goal of which is the determination of the mechanism of weak chemiluminescence accompanying the reaction of the liquid-phase oxidation of hydrocarbons.

According to the data of S. I. Vavilov (1954), the basic characteristics of luminescent particles (P^*) are: a) radiation spectrum, b) radiation yield ($\eta\rho$), c) duration (lifetime) of the excited state $\tau\rho$, d) kinetics in impulse excitation, and e) radiation polarization.

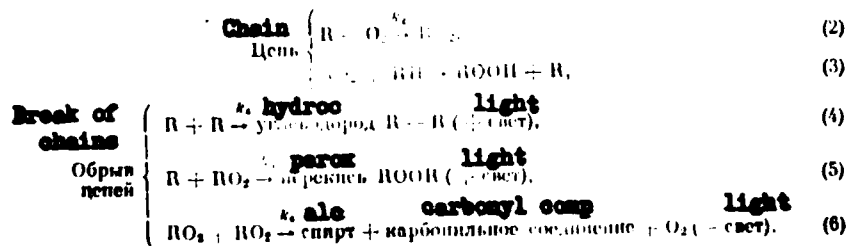
The last two characteristics in case of chemiluminescence are of no significance (the radiation is isotropic and constant in time); on the other hand, a very great role is played by data on excitation, i.e., on the speed and mechanism of the reaction.

Methods to obtain the characteristics of the excited state have been found in this work. The application of these methods has enabled us to understand the mechanism of the phenomenon. We will subsequently consider the methods and results obtained.

THE REACTION MECHANISM

The liquid-phase oxidation of hydrocarbons and their compounds is a radical chain reaction. The radicals leading the chain are the hydrocarbon radical R and the peroxy radical RO_2 . The mechanism of the first stage - - the formation of hydroperoxide $ROOH$ - - consists of the following elementary processes (Berezin, Denisov, Emanuyal', 1962).

The initiation of the chains (the appearance of the radicals R) with the speed w_1 :



It has been proved (Vasil'yev, Karpukhin, Shlyapintokh, 1959; Vasil'yev, Vichutinskiy, et al., 1961) that the excitation of luminescence occurs in exothermic processes (4), (5), (6) at the expense of energy released in the recombination (or disproportionation) of the radicals and that the intensity of luminescence is proportional to the speed of recombination, or in a stationary regime, to the speed of initiation.

A reaction proceeding in accordance with the mechanism of chain oxidation is widespread in technology and in nature. This is the oxidative processing of hydrocarbons for the purpose of obtaining valuable, oxygen-containing products; on the other hand, this constitutes undesirable processes such as the oxidation of food fats, lubricants and fuel, the oxidative destruction of polymers, etc. The chemical mechanism of reactions of the given category have been comparatively well researched. This is especially true with respect to the first stage -- the formation of hydroperoxide. Therefore, these reactions are suitable for studying the mechanism of chemiluminescence.

MEASUREMENT OF OXIDATION SPEED BY CHEMILUMINESCENT METHODS

If the substance (Y), dissociating into radicals, is introduced into an oxidating hydrocarbon, the radicals initiate the oxidation chains. The speed of radical supply (initiation speed) determines reaction speed, radical concentration, recombination speed, and luminescence intensity. Since these quantities are interconnected, chemiluminescent methods of measuring oxidation speed appear possible.

We will consider one of the methods -- the method of luminescence "oxygen decline" (Vasil'yev, Vichutinakiy, 1962). At first, the solution is saturated with oxygen, the vessel is then closed with a ground-glass stopper, and the concentration of oxygen is gradually reduced since it is expended on the oxidation of the substratum. Oxidation proceeds as long as oxygen is available, and a photomultiplier records luminescence. On the disappearance of the oxygen, the reaction is terminated. Luminescence is correspondingly and abruptly attenuated. The higher the speed of oxidation or the lower the initial concentration of oxygen, the sooner occurs the fall of luminescence. If the solubility of O_2 is known, it is not difficult to define the absolute speed of O_2 consumption:

$$w_{O_2} = [O_2] / t_{en}, \quad (7)$$

as well as the ratio of the constant of the speed of elementary reactions, which define the speed of oxidation:

$$w_{O_2} = \frac{k_1}{\sqrt{k_2}} [RH] \sqrt{u_i + \frac{1}{2} w_i}. \quad (8)$$

Another method permits the measuring of an important characteristic of the thermal dissociation of the initiator -- the energy of activation E.

The intensity of chemiluminescence is determined by the equation (Vasil'yev, Karpukhin, Shlyapintokh, 1959; Vasil'yev, Vichutinskiy, 1962):

$$I = \frac{ch}{\eta_{\text{tr}}} k_0 [\text{RO}_2]^2 = \frac{ch}{\eta_{\text{tr}}^2 c_1} \sim \frac{ch}{\eta_{\text{tr}}^2 k_0} [Y]. \quad (9)$$

The dissociation constant k_0 is changed with temperature according to Arrhenius' law: $k_0 \sim e^{-E/RT}$. While measuring (in arbitrary units) the intensity I at various temperatures and using the equation

$$\ln I = \text{const} - \frac{E}{R} \cdot \frac{1}{T}, \quad (10)$$

it is not difficult to determine the energy of activation by the inclination of the straight line.

Figure 1 presents the graphs for determining this quantity in several reactions. A check on the described and other chemiluminescent methods (Vasil'yev, Vichutinskiy, 1962, 1962a; Vasil'yev, 1962) has indicated that they are less accurate than the chemical and physical-chemical methods of measuring kinetics. These methods are especially suitable for investigating the mechanism of chemiluminescence itself, since there then is no necessity for a parallel study of corresponding reactions by other methods and on other devices.

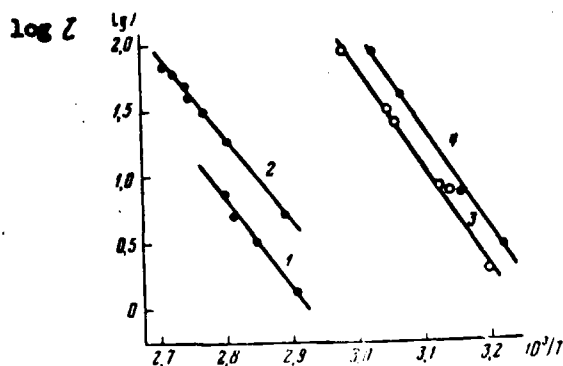


Figure 1. The temperature relationship of the intensity of chemiluminescence in the oxidation of hydrocarbons, initiated by:

- 1 - - hydroperoxide, 2,6-dimethyloctane, 2 - - tetraline hydroperoxide, 3 - - azobisisobutyronitrile, 4 - - diacetyl-peroxide.

THE DETERMINATION OF THE LIFETIME OF EXCITED STATES WITH RESPECT TO THE QUENCHING OF ALIEN SUBSTANCES

The disappearance of O_2 in a system attenuates luminescence. The attenuation occurs with low concentrations of O_2 (10^{-6} - 10^{-5} M).

With great concentrations, it can exert a quenching effect, which is linked with the physical process of excited molecule deactivation. Obviously, the greater the lifetime τ_p of the excited state, the greater is the probability of its collision with a deactivating molecule and the more noticeable is the quenching effect. On the other hand, the greater the quenching, the higher the concentration of the quencher $[O_2]$ and the constant of speed (i.e., effectiveness) k of the deactivation process:



which competes with the radiation processes



of internal deactivation



and deactivation by other quenchers Q_i



Quantitatively, this connection is expressed by the Stern-Folmer equation:

$$I_0/I = 1 + k\tau_p[O_2]. \quad (15)$$

The equation (15) is well formulated both for quenching by oxygen and for quenching by several other substances (Figure 2). An estimation of lifetime in a reaction of ethylbenzene oxidation leads to values on the order of 10^{-6} seconds (Vasil'yev, Rusina, 1963). We will note that the quantity τ_p , equaling

$$\tau_p = \frac{1}{I_p + d_p + \sum_i k_{Q_i}[Q_i]}, \quad (16)$$

depends not only on the intrinsic properties of an excited molecule, but also on environmental properties (the presence of quenchers).

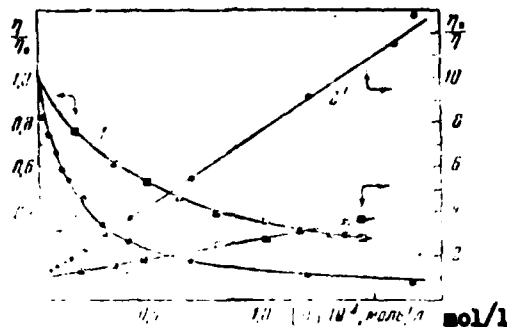


Figure 2. Reduction of the yield of chemiluminescence (η) with an increase in the concentration of the quencher (Q): oxygen (1.1') and azobisisbutyronitrile (2.2') in ethylbenzene oxidation

THE SPECTRA OF CHEMILUMINESCENCE

The intensity of luminescence in the reactions studied by us was extraordinarily low, and the measurements of the spectra were connected with great experimental difficulties. To obtain spectra, we used an image-intensifying monochromator designed specially for this purpose. In cases in which the intensity was too low, the spectral band of luminescence was determined with the use of an assembly of light filters. Both methods have been discussed in the report of R. F. Vasil'yev (1963).

In reactions of the oxidation of various hydrocarbons initiated by different substances, luminescence occupies the same band of 400-500 millimicrons. The spectrum is a broad structureless band with a slanting maximum of 420-450 millimicrons.

AN ESTIMATION OF RADIATION YIELD UPON INTENSIFYING CHEMILUMINESCENCE VIA LUMINOPHORES

The introduction into a chemiluminescent solution of substances having the capability to be energy acceptors and to luminesce (activators A) results in the addition, to the processes (11)-(14), of another process - - the transfer of energy upon the collision of P^* with A:



Radiation follows the process of energy transfer (17)



In this situation spectrum, yield, and lifetime characterize the activator molecule, and not primarily the excited particle. For example, the introduction of activators changes the spectrum: it becomes identical to the spectrum of the fluorescence of the admixture (Vasil'yev, Vichutinskiy, et al., 1963). The addition of dibromoanthracene completely removes the effect of luminescence quenching by oxygen, thereby attesting to the short duration of the excited state of A* (Vasil'yev, Rusina, 1963). Both results enable us to conclude that the state of A* is the singlet excited state of the investigated activators.

As a rule, the introduction of activators leads to a heightening of the intensity of chemiluminescence. With an increase of concentration, the intensification factor κ grows, striving toward the limit. The maximum is attained when all the particles P* transmit energy to the activator. The ratio of the maximum intensity of the activated chemiluminescence to the intensity of the initial chemiluminescence will be equal to the ratio of the radiation yields of the activator and product

$$\kappa = I_A / I_P = \eta_A / \eta_P. \quad (18)$$

If the yield η_A is known, it is possible to obtain the value of η_P from equation (18). In practice, however, the maximum value I_P is attained with such high concentrations of A that concentration self-quenching begins to appear.

Therefore, we found η_P by extrapolating for $[A] = \infty$ according to the equation

$$\frac{1}{\kappa - 1} = \frac{\eta_P}{\eta_A - \eta_P} + \frac{1}{\eta_A - \eta_P} \cdot \frac{I_P}{k_{PA}} \cdot \frac{1}{[A]}, \quad (19)$$

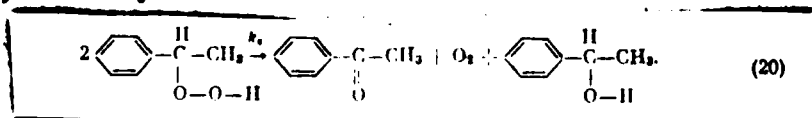
which is not difficult to obtain, considering the processes (12)-(14), (17), and (17a) with $\eta_P = f_{PTP}$ and $\eta_A = f_{ATA}$, and the quantities τ_P and τ_A are determined according to equations of the 16 type.

An estimation of η_P in reactions of the oxidation of cyclohexane and ethylbenzene lead to the value 10^{-4} - 10^{-3} (Vasil'yev, Vichutinskiy, et al., 1963; Vasil'yev, 1963).

THE IDENTIFICATION OF THE EXCITED STATE

From a study of chemistry, it is known that alcohols, carbonyl compounds, and oxygen are the products of the recombination (more precisely, the disproportionation) of the peroxy radicals.

For example, with ethylbenzene oxidation:



An analysis of the above-mentioned results indicates that the product of recombination γ - ketone in the triplet state - - is responsible for the radiation.

a. The chemiluminescence spectrum has only a single band in the 400-500 millimicron region, with a weakly expressed structure. Carbonyl compounds luminesce precisely in this band; in vapors and solutions, the oscillatory structure of the spectrum is diffused (Yermolayev, 1956).

b. From the values $\eta_p = 10^{-4} - 10^{-3}$ and $\tau_p = 10^{-6}$ seconds, it follows that $\nu = 10^2 - 10^3 \text{ sec}^{-1}$, which is characteristic of the luminescence of ketones (Yermolayev, 1956).

c. Reaction (6) is adequately exothermic (100-200 large calories per mole) for the excitation of the triplet level of acetophenone (73.15 large calories per mole).

d. Singlet excited levels of effective activators - - compounds of anthracene - - are located at 0.15-2.3 large calories per mole beneath the triplet excited level of acetophenone - - which is conducive to the transfer of energy.

e. The probability of the transfer of energy of k_{PA} increases with the introduction of heavy atoms of chlorine and bromine into the molecule of the activator.

It is noteworthy that the probability k_i of the intramolecular radiationless transition from the triplet to the basic level of these same anthracene compounds increases to the same extent (Hoffman, Porter, 1962). The attenuation of intercombination forbiddance is usually caused by spin-orbit interaction, which leads to a "mixing" of states of varying multiplicity. Thanks to the admixture of the triplet to the singlet of the activator, the transfer of energy becomes to a large extent triplet-triplet in character, which is not subject to spin limitations; and probability is increased. Theoretically, the probability of singlet-triplet transition in atoms is proportional to ζ^2 , where ζ is the matrix element of the operator of spin-orbit interaction.

For a rough estimation, it was proposed (Vasil'yev, 1963) that the effects of individual atoms be summarized in a molecule and that the quantities $\sum \zeta_i^2$, k_{PA} and k_i must be approximately reciprocally proportional. In fact, this correlation has been found to be quite exact.

THE PROBABILITY OF THE EXCITATION OF THE PRODUCT OF THE REACTION $\eta_p^{\text{exci.}}$

The speed of the recombination $w_{\text{reac.}} = w_1$, by virtue of the stability principle, is easily defined by the chemiluminescent method (Vasil'yev, Vichutinskiy, 1962 a). The intensity I can be obtained by

measuring the photocurrent and taking into account the sensitivity and configuration of the device. An estimation of the quantity $\eta_{ch} = \eta_p \eta_p^{excl.} = I/w_i$ (compare equation 1) leads to values 10^{-8} - 10^{-10} in reactions of initiated oxidation of hydrocarbons (Vasil'yev, Karpukhin, Shlyapintokh, 1959; Vasil'yev, Vichutinskiy, 1961). Considering that $\eta_p = 10^{-4}$ - 10^{-3} , we obtain $\eta_p^{excl.} = 10^{-6}$ - 10^{-4} . The quantity $\eta_p^{excl.}$ signifies the probability of the formation of a specific product of an exothermic reaction in a specific (in our case, triplet) energy state and is of great interest for the theory of elementary reactions. At the present time, there are no clear-cut ideas on how the distribution of complex molecules - - products of exothermal reactions - - occurs with respect to dissimilar energy states.

Nor is it clear what determines the transfer of energy of a chemical reaction into this or that form of product energy (electronic, oscillation, rotational, advancing). It is possible that the systematic application of chemiluminescent methods will be a promising experimental approach toward a solution of this important chemical-physical problem.

We assume that the low value of the yield of excitation is connected to a large extent to the character of product distribution with respect to energy. The nature of this distribution leads to a situation whereby the energy concentrated in a majority of molecules is inadequate for the excitation of the triplet level. Nor do we exclude the effect of an oxygen molecule which, immediately following the recombination of radicals, is found in direct proximity to products abounding in energy and can immediately deactivate them.

THE SECONDARY PROCESSES IN CHEMILUMINESCENT SOLUTIONS

The quenching and activation described in the preceding sections occurred upon the introduction of specific compounds into a solution. However, the properties of the quenchers and activators can also be the properties of the individual components of a system: initiators, solvents, hydrocarbons, admixtures, and reaction products.

The effect of secondary processes of this kind is manifested in departures from theoretically expected principles. For example, in initiated oxidation the intensity of luminescence must be proportional to the concentration of the initiator (Vasil'yev, Karpukhin, Shlyapintokh, 1959). Figure 3 makes evident that proportionality is observed only in a small number of cases. A majority of initiators play the role of quenchers, and dicyclohexylperoxidicarbonate (DTsGPK) functions as a weak initiator (Vasil'yev, Rusina, 1963).

With the speed of a process remaining constant, intensity must not be changed in time. However, with the slow disintegration of azobisisobutyronitrile (AIBN) in chlorobenzene, intensity increases

quite rapidly, and with disintegration of DTsGPK it declines. This phenomenon is linked with the accumulation of products - - activators and quenchers, respectively.

In some cases, secondary processes result in disrupting the relationship (10) between intensity and temperature (Shliapintokh [sic] et al., 1960).

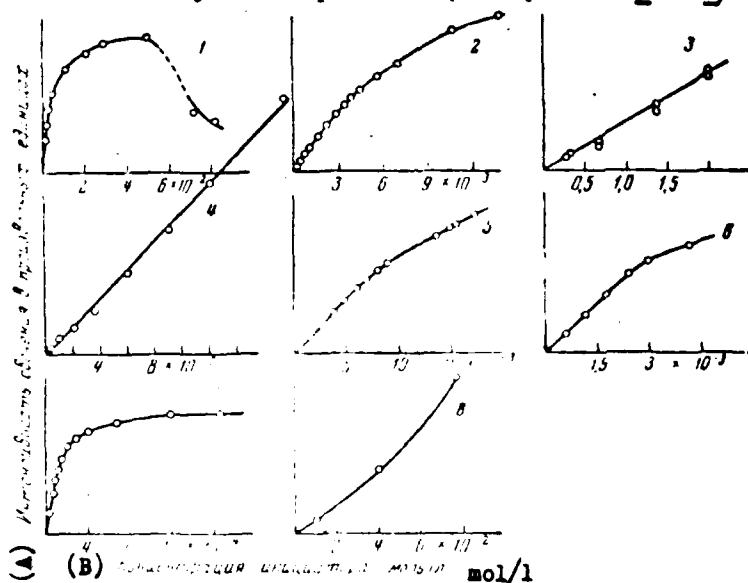


Figure 3. The relationship between the intensity of luminescence and the concentration of initiators: 1, 4, 5, 6, 7 - - azobisisobutyronitrile; 2 - - dibenzoyl peroxide; 3 - - dibutylperoxide and tributylperoxide; 8 - - dicyclohexylperoxidicarbonate. Solutions: 1, 2 - - ethylbenzene; 3 - - chlorobenzene; 4 - - benzene; 5 - - benzene + 10% cyclohexane; 6 - - acetic acid + 10% cyclohexane; 7 - - acetic acid + 0.25% ethylbenzene; (A) - - Luminescence intensity in compound units; (B) Initiator concentration, mole per liter.

In view of what has been said, it is necessary to abstain from hasty conclusions on the basis of measuring only luminescence intensity. In doubtful cases, it is essential to measure luminescence yield, i.e., a calculation of the data on the speed of that process in which excitation occurs.

On the other hand, activators specially introduced into a reactive mixture increase luminescence intensity and, correspondingly, the sensitivity of chemiluminescent methods (Vasil'yev, 1962). Moreover, they exert a "stabilizing" effect, improving yield and reducing accidental and systematic error. Figure 4 presents the results of several series of tests aimed at determining the energy of the activation of the dissociation of initiators. When the defining of this quantity yields values

(in large calories per mole) of 32.2 ± 1.7 (for AIBN) and 25.6 ± 1.4 (for DTSGIK), the values with dibromoanthracene are 31.6 ± 0.4 and 28.2 ± 0.3 , respectively. This approximates the known values 30.8-31.2 and 29.6 (Kulitski, Terman, et al., 1963). It is not difficult to explain why the activators increase the accuracy of the determination.

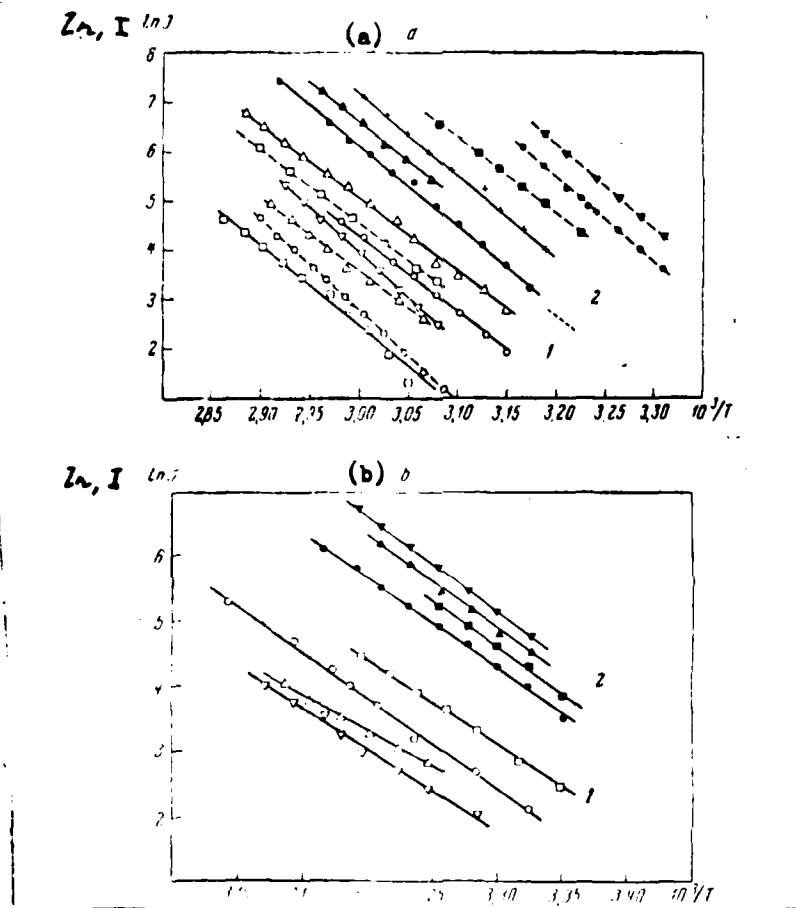


Figure 4. The relationship between chemiluminescence intensity and temperature during the oxidation of cyclohexane (broken lines) and ethylbenzene (unbroken lines) in benzene oxidation initiated by AIBN.

(a) ($6.1 \cdot 10^{-3}$ mole per liter) and by DTSGPK (b) ($1.75 \cdot 10^{-3}$ mole per liter).
 1 - - without an activator, 2 - - with 9,10-dibromoanthracene ($6.0 \cdot 10^{-3}$ mole per liter).
 For improving visibility, the straight lines have been shifted somewhat toward a vertical position

In the absence of a weak-radiation activator, processes with "natural" quenchers and activators compete successfully. The effect of these processes can depend on temperature and, consequently, impinge on the temperature-intensity relationship. Then introducing an activator, we create more specific conditions for the transformation of the energy of the excited product into light: now, energy proceeds along the channel $P^* \rightarrow A^* \rightarrow h\nu_A$, and other secondary processes cannot withstand the competition. The coincidence of the values of activation energy presented in literature with those measured with respect to activated chemiluminescence indicates that the transfer of energy is not accompanied by a surmounting of the energy barrier by more than 0.3-0.5 large calories per mole (the measurement error).

THE NATURE OF THE SPECIAL CONNECTION BETWEEN CHEMILUMINESCENCE AND OXIDATION

As is known, chemiluminescence is observed almost exclusively in oxidation reactions (Rid, 1960). That astonishing interconnection of chemiluminescence and oxidation was established for the first time three centuries ago by Robert Boyle, who had observed that the luminescence of bacteria was attenuated upon air evacuation and was renewed with its former force upon the introduction of air under the bell of an air pump. Subsequently, this characteristic of chemiluminescence has been emphasized by many authors. However, this feature was not theoretically explained. The intensification of chemiluminescence by oxygen looked strange - - all the more so because, through tests on photoluminescence, oxygen was well known as a quencher, a deactivator of excited states.

In the Chemical Physics Institute of the USSR Academy of Sciences, a weak luminescence was recorded in a number of reactions taking place without O_2 , e.g., in reactions of the thermal dissociation of organic substances. Here, excitation occurred upon the recombination of radicals R (4) at the expense of the energy of newly formed connections. However, the introduction of O_2 even in these cases constantly led to an intensification of chemiluminescence (Vasil'yev, Vichutinskiy, et al., 1961). It was demonstrated (Vasil'yev, Vichutinskiy, et al., 1961, 1962, 1962 a) that in radical reactions the intensification of chemiluminescence upon the introduction of oxygen was of a chemical nature, being connected with the appearance of peroxy radicals (2) and higher yields of luminescence upon the recombination of peroxy radicals (6).

The dissimilarity of the luminescent yields in the processes (6) and (4) is explained by the difference in spectroscopic properties of the radiating particles - - the products of the recombination of the radicals RO_2 and, correspondingly, the radicals R. For the first time, there is an oxygen-containing molecule (ketone, aldehyde, etc) which luminesces in the visible or near the ultraviolet band; others do not luminesce nearly as well. Consequently, the products of reaction (6)

are capable of transforming energy into light more effectively than the products of reaction (4). The higher the concentration of O_2 , the greater is the contribution of process (6) to general recombination, and the higher must be luminescence intensity.

The quenching effect of O_2 , an effect of a purely physical nature, is also observed in chemiluminescence; it has been discussed above. This effect is manifested much less sharply and with large concentrations of O_2 .

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