

Shlyapintokh, I. YA.

Initiation of the oxidation of 2,7-dimethyloctane by free radicals formed in the photolysis of salts of metals with a variable valence. I. Ya. Shlyapintokh and N. M. Emanuel. *Izv. Akad. Nauk S.S.S.R., Otd. Khim. Nauk* 1957, 782-6. The photolysis of the stearates of  $Cu^{++}$  and  $Fe^{++}$ , when carried out in 2,7-dimethyloctane at elevated temp. (123°) in the presence of mol. O, increases the rate of oxidation. The photolysis of  $Fe(C_2H_5O_2)_2$  forms  $Fe(C_2H_5O_2)_3$  (I) and the free radical  $C_2H_5O_2$ , which was observed from the evolution of  $CO_2$  in the photolysis of this salt in a N atm. The catalytic effect of the photolysis reaction was attributed to the reaction of the radical  $C_2H_5O_2$ , which is formed from the decomn. of  $C_2H_5O_2$ , and to the reactions of I with peroxide compds. J. Rovtar Leach

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*Shlyapintokh, I. Ya.*  
SHLYAPINTOKH, I. Ya.

State Institute for the Design and Planning of Iron and Nonferrous  
Ore Mining Industries. Shakt.stroi. no.11:32-33 N '57. (MIRA 10:12)

1. Nachal'nik tekhnicheskogo otdela instituta Girporuda.  
(Iron mines and mining) (Nonferrous metal industries)  
(Research, Industrial)

SHLYAPIINTOKH, I. Ya.

AUTHORS: Tsepalov, V. F., Shlyapintokh, I. Ya. 20-4-31/51

TITLE: Note on the Intermediate Products in Redox Photoreactions of Xanthine Dyes (O promezhutochnykh produktakh v okislitel'novosstanovitel'nykh fotoreaktsiyakh ksantenovykh krasiteley).

PERIODICAL: Doklady AN SSSR, 1957, Vol. 116, Nr 4, pp. 641-644 (USSR)

ABSTRACT: The xanthine dyes eosine, erythrosine and bengal pink are frequently utilized photosensitizer of oxydation and polymerization processes. A potentiometer method was employed for studying the photo reduction and photo oxydation of xanthine dyes. In the present paper the measurements of the photo galvanic effect permitted the recording of the formation of the intermediate products in the redox- reactions of some dyes. The experiments were conducted in a container with platinum electrodes. The authors established the following facts in complete accordance with the results obtained from chlorophyll theophitine (feofitin) and other pigments. The illumination of an alcoholic solution or of a pyridine solution of a xanthine dye ( $C = 10^{-6} - 10^{-3}$  Mol/l) shifts the electrode potential towards the positive in the presence of oxygen.

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An illumination in the presence of reducing substances (alcohol, pyridine, ascorbinic acid, aldehyde) shifts the electrode potential towards the negative. A diagram illustrates the kinetic curves of the modification of potential of a platinum electrode, which is immersed in a pyridine solution of eosine. The measurements were conducted with different light intensities from  $I = 1$  to  $I = 0,08$ . On illumination the potential decreases, reaches a certain minimum, the increases again and returns to the original value. The modification of the photo potential observed here is connected with the existence of an intermediate product. The considerations institute by the authors also explain the dependence of the kinetics of the modification of the potential on the concentration of the dye, which has been observed experimentally. An increase of concentration of eosine shows in general the same influence on the kinetics of the process as an increase of the light intensity. On a cooling down the velocity of the potential reversal decreases quickly. The character of the dependence of the kinetics of the modification of the potential on temperature

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distinctly speaks in favour for a stage-like character  
of the reduction process. Finally, a few words are said  
concerning this reaction at various pigments.  
There are 4 figures, and 3 Slavic references.

PRESENTED: April 12, 1957, by A. N. Terenin, Academician

SUBMITTED: February 7, 1957

AVAILABLE: Library of Congress

Card 3/3

AUTHORS: Selivanov, V. V., Shlyapintokh, I. Ya. 76-32-3-27/43

TITLE: The Thermodynamic Properties of Air in Thermal Ionization and the Shock Wave (Termodinamicheskiye svoystva vozdukhа pri termicheskoy ionizatsii i udarnaya volna)

PERIODICAL: Zhurnal Fizicheskoy Khimii, 1958, Vol 32, Nr 3, pp 670-678 (USSR)

ABSTRACT: According to Davies (reference 1), full dissociation of the air is practically obtained at temperatures of 10 000-15 000°C, whereas at still higher temperatures, thermal radiations play an important part. The data of the thermodynamic properties of air at several 1 000°C are to be found in the papers by Davies (reference 1), M. P. Vukalovich (reference 2), Ya. B. Zel'dovich and A. I. Polyarnyy (reference 3), as well as L'ymis and El'be (reference 4), whereas the present work performs determinations of the thermodynamic properties of air at temperatures where the dissociation is finished and where only ionization and radiation take place. The

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Ionization and the Shock Wave

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investigations were not made in natural air, but in a mixture of 79.1% nitrogen and 20.9% oxygen (by volume). In the calculation of the statistical sums, it is emphasized that the number of energy levels shall be limited, for the solution of this problem is considered complicated and the selection of the number of levels is practically arbitrary. In the present work the number 10 was never surpassed. It is said that a wrong selection of numbers exerts little influence upon the final results. The obtained experimental results show that at temperatures of 200,000 - 400,000 °C the gas mixture mainly consists of free electrons and nuclei of nitrogen and oxygen with 2 helium electrons, this being explained by the higher dissociation energy of the two last-mentioned electrons. The results of the calculation of the thermodynamic quantities are given in tables. From the obtained results and diagrams follows that a great influence of the dissociation and ionization upon the front parameters of the shock wave is exists, the latter propagating

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with velocities up to 115 km/sec. Finally the authors thank Professor  
D. A. Frank-Kamenetskiy and Ya. B. Zel'dovich, Corresponding Member.  
There are 4 figures, 6 tables, and 10 references, 8 of which are  
Soviet.

ASSOCIATION: Akademiya nauk SSSR, Institut khimicheskoy fiziki, Moskva  
(AS USSR Moscow Institute of Chemical Physics)

SUBMITTED: December 28, 1956



SHLYAPINTOKH, L.

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12 no.5:29 My '55. (MIRA 8:8)

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СНЛ-77/11/1955, 1-10

KIPAYEV, Valentin Yevgen'yevich; PETROV, Vadim Konstantinovich;  
SHLYAPINTOKH, Lev Samoylovich; KUKHNOV, D.A., dotsent,  
kandidat ~~tehnicheskikh nauk~~, redaktor; KOPTEVSKIY, D.Ya.  
redaktor; OSTRIROV, N.S., ~~tehnicheskij~~ redaktor

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*Список авторов и редакторов*  
KITAYEV, Valentin Yevgen'yevich, kandidat tekhnicheskikh nauk; PETROV,  
Vadim Konstantinovich, inzhener; SHLYAPINTOKH, Lev Samoylovich,  
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skiy redaktor

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*SHLYAPINTOKH, L.S.*

GRAMMATIKATI, Vera Mikhaylovna; PETROV, Vadim Konstantinovich; SHLYAPINTOKH  
Lev Samoylovich; BILINSKIY, M.Ya., red.; BARANOVA, N.N., tekhn.red.

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~~SHLYAPINTOKH, I. S.~~

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ROGACHEV, F.V., red.; RAKOV, S.I., tekhn.red.

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L.P., red.; SMIRNOVA, M.I., tekhn. red.

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SHLYAPINTOKH, Lev Samoylovich; SIMONOV, A.F., nauchnyy red.;  
IOFFE, M.L., red.izd-va; TOKER, A.M., tekhn.red.

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(MIRA 14:3)

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nauchn. red.; SIL'VERSTROVICH, G.A., red.; DORODNOVA,  
L.A., tekhn. red.

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trotekhniki s osnovami promyshlennoi elektroniki. Moskva,  
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PETROV, Vadim Konstantinovich [deceased]; SHLYAPINTOKH, Lev  
Samoylovich; GETLING, B.V., nauchn. red.; MUPKINA,  
V.G., red.

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industrial electronics fundamentals] Sbornik zadach po  
elektrotekhnike s osnovami promyshlennoi elektroniki.  
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(MIRA 18:7)





5(4)

AUTHORS:

Tsepalov, V. F., Shlyapintokh, V. Ya.

SOV/62-59-4-10/42

TITLE:

Mechanism of the Photoreduction of Xanthene Dyestuffs  
(Mekhanizm reaktsii fotovosstanovleniya ksantenovykh krasiteley)

PERIODICAL:

Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk,  
1959, Nr 4, pp 637-643 (USSR)

ABSTRACT:

The photoreduction of xanthene dyestuffs consists in a transformation of the dyestuff into a colorless leuco compound; the dyestuff is completely bleached out when the reaction is completed. Eosine, erythrosine, chemically pure Bengal pink and ("ch.d.a") ascorbic acid were used in the present work whereas ethanol and pyridine were used as solvents. A typical kinetic curve of the potential change of the platinum electrode dipped in the dyestuff solution exposed to light is shown in figure 1. It is seen that the potential changes quickly in the negative direction upon exposure to light to reach the minimum and return to the initial value. This course has been ascribed to the presence of an intermediate product formed during the reduction of the eosine. With the aid of potentiometric measurements it has been found that the intermediate products formed during the

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reduction of the dyestuffs are sufficiently stable and have a life of  $-30^{\circ}$  to  $-40^{\circ}$  minutes. In view of the data found on the life and on the conditions under which the highest concentrations of intermediate products can be obtained the photoreduction of the xanthene dyestuffs has been subjected to spectral analysis. The spectra of the intermediate products are shown in figure 3. As the spectrum of an intermediate product depends neither on the dyestuff nor on the reducing agent this compound can be assumed not to form any complex with the dyestuff or the reducing agent. Figure 4 shows the kinetic curves of the intermediate products of eosine and the potential change of the electrode determined during an experiment conducted at room temperature. These data indicate that the concentration of the intermediate product at the time when the light is removed is  $c_{EN} \geq 7.8 \cdot 10^{-6}$  or 20% of the initial concentration of the eosine. The highest concentration reaches 35%. Based on the same data the molar absorption coefficient of the intermediate product has been obtained  $(E_{EN})_{427} \leq 1.1 \cdot 10^4$  l/mole-cm. As is apparent from figure 5 the highest optical density of the inter-

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mediate product at  $-35^{\circ}$  reaches 0.62, which means that it is about five times higher than at room temperature. The estimation of the maximum concentration in view of the amount of dye-stuff regenerated after the removal of light has led to the values  $c_{EN} \geq 42\%$  of the initial eosine and

$(E_{EN})_{427} \leq 4.4 \cdot 10^4$  l/mole-cm. The cause for the great variation of the  $E_{EN}$  values with temperature has not been clarified.

It becomes evident from figure 6 that the potential reaches the zero level more quickly at a higher concentration of the reducing agent. This shows that the intermediate product is consumed more quickly than it is formed. There are 7 figures and 5 references, 2 of which are Soviet.

ASSOCIATION: Institut khimicheskoy fiziki Akademii nauk SSSR (Institute of Chemical Physics of the Academy of Sciences, USSR)

SUBMITTED: July 10, 1957

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5(3), 5(4), 24(7)

SOV/51-7-1-19/27

AUTHORS: Bubnov, N.N., Kibalko, L.A., Tsepalov, V.F. and Shlyapintokh, V.Ya.

TITLE: On the Nature of the Intermediate Product in the Reaction of Photo-reduction of Eosin (O prirode promezhtochnogo produkta v reaktsii fotovosstanovleniya eozina)

PERIODICAL: Optika i spektroskopiya, 1959, Vol 7, Nr 1, pp 117-119 (USSR)

ABSTRACT: Eosin solution in pyridine ( $10^{-4}$  mole/litre) was photoreduced in the presence of ascorbic acid ( $10^{-3}$  mole/litre). A SVDSH-250 lamp was used as the light source and the reaction was studied using an electron-paramagnetic-resonance (e.p.r.) spectrometer with high-frequency modulation of the magnetic field. The e.p.r. spectrum (the upper figure on p 118) was a triplet with the component intensities in the ratio 1:2:1 (the hyperfine-structure splitting was  $\Delta H = 4.6 \pm 0.2$  oersted). The e.p.r. spectrum was due to an intermediate product in the photo-reduction reaction; the shape of the spectrum confirmed earlier

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Eosin

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suggestions (Refs 1, 2) that (1) the intermediate product is eosin semiquinone, and that (2), in the photochemically-active state, eosin is a metastable biradical. There are 2 figures and 10 references, 4 of which are Soviet, 3 German, 2 English and 1 French.

SUBMITTED: November 25, 1958

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24 (7)

AUTHORS:

Bubnov, N. N., Tsepalov, V. F.,  
Shlyapintokh, V. Ya.

SOV/48-23-10-36/39

TITLE:

The Spectra of Paramagnetic Electron Resonance of Eosin  
Semiquinone in a Live Leaf

PERIODICAL:

Izvestiya Akademii nauk SSSR. Seriya fizicheskaya, 1959,  
Vol 23, Nr 10, pp 1265 - 1266 (USSR)

ABSTRACT:

The present paper intends to explain the nature of the intermediate products in the photochemical reactions of eosin and chlorophyll. The investigations were carried out at room temperature with high-frequency modulation of the magnetic field. Method and apparatus are described in references 1 and 2. First, some results concerning the photoreduction of eosin are discussed. This reaction consists in the transformation of the dye into a leuco-compound and has already been potentiometrically and spectroscopically investigated (Refs 3,4). The authors assumed that a comparatively stable intermediate product is formed (semiquinone dye), which may have a life of several seconds at room temperature. An investigation of the paramagnetic electron resonance spectrum of eosin (solvent: piridine, reducer: ascorbic acid) showed a

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The Spectra of Paramagnetic Electron Resonance of SOV/48-23-10-36/39  
Eosin Semiquinone in a Live Leaf

triplet splitting (intensity ratio 1:2:1,  $\Delta H = 4.6 \pm 0.2$  Gs) which is caused by the interaction between the unpaired electron and two protons. The photochemical reaction which develops by way of a biradical, is shown schematically and has already been described by Schenck (Ref 5). The authors of the present paper were the first to investigate the resonance spectrum of a live leaf. A leaf of *agrophyrum repens* was used for this purpose. The resonance signal showed a doublet, hyperfine splitting amounted to  $\Delta H = 1.8 \pm 0.2$  Gs. There are 5 references, 4 of which are Soviet.

ASSOCIATION: Institut khimicheskoy fiziki Akademii nauk SSSR (Institute of Chemical Physics of the Academy of Sciences, USSR)

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5(4)

SOV/20-124-4-43/67

AUTHORS: Tsepalov, V. F., Shlyapintokh, V. Ya.

TITLE: The Determination of the Elementary Constants of the Reaction of the Oxidation of Ethyl-benzene by the Method of Intermittent Illumination (Opredeleniye elementarnykh konstant reaktsii okisleniya etilbenzola metodom preryvistogo osveshcheniya)

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 124, Nr 4, pp 883-886 (USSR)

ABSTRACT: According to present-day concepts, the oxidation of hydrocarbons in the liquid phase develops according to a chain mechanism accompanied by the formation of hydrogen peroxide as the primary stable product of oxidation. At moderate temperatures hydrogen peroxide is also the final product, and in this case the reaction develops in accordance with the following scheme: Production of radicals  $\dot{R}$  or  $\dot{RO}_2$ , rate  $w_i$ ;

(I). Continuation of the chain  $\dot{R} + O_2 \xrightarrow{k_2} \dot{RO}_2$  (II);

$\dot{RO}_2 + RH \xrightarrow{k_3} RO_2H + \dot{R}$  (III).  $2\dot{R} \xrightarrow{k_4} \text{inactive products}$

(IV),  $\dot{R} + \dot{RO}_2 \xrightarrow{k_5} \text{inactive products (V)}$ ;  $2\dot{RO}_2 \xrightarrow{k_6} \text{inactive products (VI)}$ . Here RH denotes the hydrocarbon,  $\dot{R}$  - an alkali

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SOV/20-124-4-43/67

The Determination of the Elementary Constants of the Reaction of the Oxidation of Ethyl-benzene by the Method of Intermittent Illumination

radical, and  $\dot{R}O_2$  .. a peroxide radical. Next, an expression is written down for the rate of the reaction for this scheme for the case of long chains, and is then specialized for the case of sufficiently high concentrations  $[O_2]$  of oxygen:

$$\frac{d[O_2]}{dt} = w_i^{1/2} k_3 k_6^{-1/2} [RH].$$

In the case of short chains

the initiation rate  $w_i$  must be added to the right part. The last-mentioned equation contains 3 unknown quantities  $w_i$ ,  $k_3$  and  $k_6$ , and accordingly, three independent relations are required for the separate determination of these three quantities. The theory of the method of continuous illumination of such a decomposition has already been discussed in an earlier paper (Ref 3). By means of this method it is possible to measure the mean life of this chain, or, which is the same thing, the mean life  $\tau$  of the radical. Formulas for the

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determination of  $\tau$  are written down. Carrying out of the experiments is described in short. The rate of reaction is determined from the absorption of oxygen in a vacuum device with automatic recording. The light source used was a mercury lamp SVDSH-250, which was fed with direct current. The next chapter deals with the determination of the initiation rate. The experimentally determined dependence of  $d[O_2]/dt$  on

the concentration  $1/[B]$  of the inhibitor is shown by a diagram. The straight lines for 2 inhibitors at different temperatures intersect at one and the same point, which is indicative of the fact that the additions of these inhibitors do not modify the initiation rate itself and that the latter also does not depend on temperature. This fact was used for the direct measurement of the quantity  $w_i$ . For this purpose the dependence of the reaction rate on temperature was determined. In the case of sufficiently low temperatures ( $5-15^\circ$ ) the reaction rate does not depend on temperature. Within this temperature range the length of the chain is near zero, and it holds that  $d[O_2]/dt = w_i$ . The values of  $w_i$  determined by the inhibitor method and from the temperature-dependence

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The Determination of the Elementary Constants of the Reaction of the Oxidation of Ethyl-benzene by the Method of Intermittent Illumination

of the reaction rate are in practical agreement. Furthermore, the initiation rate was determined by means of the second method, because more accurate results may be obtained in this way within a shorter time. In the last part of this paper the life-times of peroxide radicals are determined. There are 4 figures, 1 table, and 6 references, 1 of which is Soviet.

ASSOCIATION: Institut khimicheskoy fiziki Akademii nauk SSSR  
(Institute for Chemical Physics of the Academy of Sciences, USSR)

PRESENTED: October 11, 1958, by V. N. Kondrat'yev, Academician

SUBMITTED: September 20, 1958

Card 4/4

5(4)

AUTHORS: Vasil'yev, R. F., Karpukhin, O. N., SOV/20-124-6-21/55  
Shlyapintokh, V. Ya., Emanuel', N. M., Corresponding Member,  
AS USSR

TITLE: Gas Initiation by Ozone in the Reaction of the Oxidation of  
Isodecane and the Chemiluminescence Connected With It  
(Gazovaya iniciatsiya ozonom v reaktsii okisleniya izo-  
dekana i svyazannaya s nim khemilyuminestsentsiya)

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 124, Nr 6, pp 1258-1260  
(USSR)

ABSTRACT: The present paper deals with the stage of initiation by ozone  
in segregated form, i.e. the authors investigate such phenom-  
ena and processes as occur during the short action of the  
initiator. Isodecane (2,7-dimethyl-octane) was used as test  
object. Preliminary tests showed that if ozone is blown past  
during a short time the reaction is accelerated considerably.  
The authors recorded a weak glow which was produced during  
the bubbling of oxygen (containing 2-3 % ozone) by isodecane.  
This isodecane was in a glass oxidation cell at temperatures  
of 20-90°. By glow the photomultiplier FEU-19 served as an  
indicator of the glow. The photoelectric current was recorded

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Gas Initiation by Ozone in the Reaction of the SOV/20-124-6-21/55  
Oxidation of Isodecane and the Chemiluminescence Connected With It

by means of the electronic potentiometer EPPV-51. The first diagram shows the intensity of glow as a function of time during the uninterrupted blowing-through of ozone and isodecane at a temperature of 55°. Intensity increases gradually and, after 2.5 hours, it attains a maximum after which it gradually decreases. As soon as the adding of ozone is interrupted, the glow immediately vanishes in all stages of the reaction. If ozone is again supplied, the previous intensity is quickly restored. According to these results the glow is caused in the interaction between ozone and a compound, which was formed already before this interaction as the result of a reaction of ozone with carbon. The above mentioned intensity maximum indicates that the concentration of this hypothetical compound passes through a maximum. In this case the kinetics of the accumulation of this compound agrees with the kinetics of the accumulation of the intermediate product in the case of successive chemical reaction. An other possibility of explaining the phenomena discussed is rejected on the grounds of being unsuited. A further proof of the intermediate character of the product of primary interaction

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Oxidation of Isodecane and the Chemiluminescence Connected With It

with ozone was supplied by experiments carried out with higher temperatures. Thus, the interaction between ozone and normal hydrocarbons at moderate temperatures is a complicated process in the course of which a relatively stable intermediate compound is formed. There are 3 figures and 4 Soviet references.

ASSOCIATION: Institut fizicheskoy khimii Akademii nauk SSSR (Institute of Physical Chemistry of the Academy of Sciences, USSR)

SUBMITTED: October 29, 1958

Card 3/3

5(4)

AUTHORS: Vasil'yev, R. F., Karpukhin, O. N., SOV/20-125-1-28/67  
Shlyapintokh, V. Ya.

TITLE: Chemiluminescence in Reactions of Thermal Decomposition  
(Khemiyluminesentsiya v reaktsiyakh termicheskogo raspada)

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 125, Nr 1, pp 106-109  
(USSR)

ABSTRACT: The present paper describes the results obtained from experiments, in which a very weak luminescence was detected. The luminescence in question occurs with the decomposition of some organic compounds in hydrocarbons as solvents. A figure illustrates the scheme of the apparatus used for recording the luminescence. The reaction takes place in a cuvette placed in a transparent chamber. The cuvette is enclosed by a water-heated outer glass wall which acts as a thermostat. The image of the cuvette is then projected onto the photocathode of the photomultiplier FEU-19, and the current supplied by the latter is recorded by an electronic potentiometer EPPV-51. The authors investigated the thermal decomposition of the hydrogen peroxides of Tetralin; 2,7-dimethyloctane; isopropylbenzene; benzoyl peroxide and isozobutyronitryl. Chlorobenzene was used as a

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SOV/20-125-1-28/67

## Chemiluminescence in Reactions of Thermal Decomposition

solvent in all reactions. A table specifies the conditions under which the reaction was investigated. According to the experimental results the intensity of luminescence increases with rising temperature. In the case of the hydrogen peroxides of 2,7-dimethyl octane and of tetralin as well as of benzoyl peroxide, the law  $I \sim \exp(-A/RT)$  holds with good accuracy for the intensity of luminescence. For these substances the temperature coefficients amount to  $29.3 \pm 1.0$ ;  $26.5 \pm 1.5$ ;  $31.9 \pm 1.0$ . At a given temperature, intensity remains unvaried for many hours; however, there is a limit temperature for each substance, beyond which intensity decreases according to an exponential law. The existence of a chemiluminescence signifies that the reaction zone contains excited particles. In all of the chemical systems investigated by the authors, only recombination reactions of radicals bring about an excitation. The following dependence on time and temperature applies for the intensity of luminescence:  $I \sim e^{-E/RT} e^{-kt}$ . Most of the reactions investigated here agreed well with this law. The temperature coefficients  $A$  determined by the authors are in agreement with the activation energies of the

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Chemiluminescence in Reactions of Thermal  
Decomposition

SOV/20-125-1-28/67

decomposition of the corresponding substances. Chemiluminescence reactions may widely occur even in simple reactions. The authors probably observed the luminescence of primary excited particles. There are 3 figures, 1 table, and 6 references, 2 of which are Soviet.

ASSOCIATION: Institut khimicheskoy fiziki Akademii nauk SSSR (Institute of Chemical Physics of the Academy of Sciences, USSR)

PRESENTED: October 29, 1958, by V. N. Kondrat'yev, Academician

SUBMITTED: September 20, 1958.

Card 3/3

ENTELIS, S.G.; SHLYAPINTOKH, V.Ya.; KARPUKHIN, O.N.; NESTEROV, O.V.

Chemiluminescence in the reaction involving the formation of nylon when the process is carried out in solution and at the phase boundary. Vysokom. soed. 2 no. 3:463 Mr '60.  
(MIRA 13:11)

(Nylon) (Luminescence)

86408

S/062/60/000/008/015/033/XX  
B013/B055

5.1190

2209, 1208, 1274

AUTHORS:

Vasil'yev, R. F., Kozlova, Z. G., Chuchukina, L. G.,  
Shlyapintokh, V. Ya., and Emanuel', N. M.

TITLE:

On the Change in Catalytic Activity of Nickel Stearate  
During the Oxidation of Ethyl Benzene

PERIODICAL:

Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk,  
1960, No. 8, pp. 1337-1341

TEXT: The present publication treats a phenomenon observed during the nickel-distearate catalyzed oxidation of various hydrocarbons. The authors observed that in these reactions the maximum concentration of the hydroperoxide fairly equals its concentration in an uncatalyzed reaction. It was shown that the anomalous course of the kinetic curve of the hydroperoxide during the oxidation of ethyl benzene is connected with an inactivation of the catalyst. Various experiments were made to establish the cause of the reduced activity of the catalyst during the oxidation process (Figs. 3, 4). These experiments lead the authors to assume that products reacting with the catalyst and reducing its activity are formed during  
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86408

On the Change in Catalytic Activity of Nickel S/062/60/000/008/015/033/XX  
Stearate During the Oxidation of Ethyl Benzene B013/B055

the reaction. Since acids accumulate during the oxidation of the decomposition products of hydroperoxide, it seems likely that these very acids inactivate the catalyst, e.g. by forming insoluble salts (Refs. 2-4). Experiments performed in this direction showed that the reduced activity of the catalyst is indeed related to its reaction with these acids (Fig. 5). The established reduction of catalyst activity during the reaction permits a simple explanation for the accumulation of peroxides during the nickel-stearate catalyzed reaction (Figs. 1, 2). Till the maximum peroxide concentration is reached, the nickel salt is completely inactivated. The reaction is then practically uncatalyzed and the maximum peroxide concentrations are therefore in agreement. At the same time the maximum concentration is reached more quickly in the presence of nickel stearate since the latter has a strong catalytic effect at the outset of the reaction. The results of this investigation furnish further proof that in the catalytic oxidation of hydrocarbons metal salts are no catalysts but rather initiators of the process. Their activity, and frequently also the mechanism of their effect, change during the process. The observed reaction kinetics therefore reflect not only the properties of the reacting system, but also the changes in the activity and action of the catalyst in the

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On the Change in Catalytic Activity of Nickel Stearate During the Oxidation of Ethyl Benzene <sup>86408</sup> 5/002/60/000/008/015/033/XX B013/B055

individual stages of the reaction. In studies of the catalytic mechanism, stabilization of the catalyst is particularly important. This would considerably facilitate the explanation of the mechanism of the catalytic effect of metal salts. There are 6 figures and 4 references: 3 Soviet and 1 British.

ASSOCIATION: Institut khimicheskoy fiziki Akademii nauk SSSR  
(Institute of Chemical Physics of the Academy of Sciences USSR) ✓

SUBMITTED: February 18, 1959

Card 3/3

BUBNOV, N.N.; KRASNOVSKIY, A.A.; UMRIKHINA, A.V.; TSEPALOV, V.E.;  
SHLYAPINOTOKH, V.Ya.

Electron paramagnetic resonance spectra observable during the  
illimination of plant leaves and photoreduction of chlorophyll  
and its analogues. Biofizika 5 no. 2:122-126 '60. (MIRA 14:4)

1. Institut khimicheskoy fiziki AN SSSR i Institut biokhimii im.  
A.N. Bakha AN SSSR, Moskva.

(CHLOROPHYLL)  
(PARAMAGNETIC RESONANCE AND RELAXATION)

VASIL'YEV, R.F.; KOZLOVA, Z.G.; CHUCHUKINA, L.G.; SHLYAPINTOKH, V.Ya.;  
EMANUEL', N.M.

Change of the catalytic activity of nickel stearate in the process  
of ethylbenzene oxidation. Izv.AN SSSR Otd.khim.nauk no.8:1337-  
1341 Ag '60. (MIRA 15:5)

1. Institut khimicheskoy fiziki AN SSSR.  
(Catalysts, Nickel) (Benzene) (Oxidation)

S/076/60/034/007/040/042/XX  
B004/B068

AUTHORS: Entelis, S. G., Shlyapintokh, V. Ya., Karpukhin, O. N.,  
and Nesterov, O. V.

TITLE: Chemiluminescence in Reactions of Acid Chlorides With  
Amines and Ketones

PERIODICAL: Zhurnal fizicheskoy khimii, 1960, Vol. 34, No. 7,  
p..1651

TEXT: It was established by the authors that the acylation of amines  
and ketones by organic acid chlorides is accompanied by chemilumines-  
cence. Luminescence can be observed with an ФЭУ-29 (FEU-29) photomulti-  
plier sensitive to the range from 350 - 610 mμ. The following reactions  
of the components dissolved in organic solvents are mentioned:

✓

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Chemiluminescence in Reactions of Acid Chlorides With Amines and Ketones S/076/60/034/007/040/042/XX  
B004/B068

| Reaction                        | Signal*                                       |
|---------------------------------|---|
| $C_6H_5NH_2 + C_6H_5COCl$       | 0 (dissolved in chlorobenzene)                |
| $C_6H_5NH_2 + C_6H_5COCl$       | 0.55 (dissolved in benzene)                   |
| $C_6H_5NH_2 + C_6H_5COCl$       | 2-5.5 (dissolved in acetone)                  |
| $C_6H_5NH_2 + ClOC(CH_2)_4COCl$ | 6.5 (amine in acetone, chloride in toluene) ✓ |
| $C_6H_5NH_2 + ClOC(CH_2)_4COCl$ | 7 (amine in benzene, chloride in toluene)     |
| $CH_3COCH_3 + C_6H_5COCl$       | 0.35 (ketone in acetone, chloride in benzene) |
| $CH_3COCH_3 + ClOC(CH_2)_4COCl$ | 0.7 (ketone in acetone, chloride in toluene)  |
| $C_6H_5NH_2 + HCl$              | 0.01 (dissolved in chlorobenzene)             |

\* The intensity of the signal is expressed in relative units. About  $2 \cdot 10^4$  quanta/sec.cm<sup>3</sup> of the reaction volume are taken as unit. There is 1 table.

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Chemiluminescence in Reactions of Acid Chlorides With Amines and Ketones S/076/60/034/007/040/042/XX  
B004/B068

ASSOCIATION: Akademiya nauk SSSR, Institut khimicheskoy fiziki, Moskva  
(Academy of Sciences USSR, Institute of Chemical Physics,  
Moscow)

SUBMITTED: December 29, 1959

✓

Card 3/3

VASIL'YEV, R.F.; SHLYAPINTOKH, V.Ya.; EMANUEL', N.M.

Mechanism of the initiating action of nitrogen dioxide in the  
oxidation of 2,7-dimethyloctane by molecular oxygen. Izv. AN  
SSSR, Otd. khim. nauk no.2:218-225 F '61. (MIRA 14:2)

1. Institut khimicheskoy fiziki AN SSSR.  
(Octane) (Nitrogen oxide)

5 118D

2209 1257 1274

23587  
S/062/61/000/005/002/009  
B118/B208

AUTHORS: Korsun, A.G., Shlyapintokh, V. Ya., and Emanuel, N. M.

TITLE: Catalytic decomposition of ethyl benzene hydroperoxide

PERIODICAL: Akademiya nauk SSSR. Izvestiya. Otdeleniye khimicheskikh nauk, no. 5, 1961, 788 - 796

TEXT: The systems consisting of a metal salt of variable valence and a peroxide are frequently used as catalysts in the oxidation of hydrocarbons and as initiators in the radical polymerization. The mode of action of such systems is based on the fact that they produce free radicals and thus increase the initiation rate of the chains. The salt catalysts undergo a change during the oxidation process in the oxidation of hydrocarbons. During the reaction the valence of the metal changes, and complexes are formed from the metal salt and the reaction products with the metal salt being precipitated in certain cases. The catalyst may play a part not only in the initiation of the chains, but also in the chain rupture and, apparently, in the elongation of the chains. Such changes of the catalyst and its manifold functions highly complicate the reaction kinetics and

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S/062/61/000/005/002/009  
B118/B208

Catalytic decomposition of...

make it difficult to understand the mechanism of the catalytic effect of metal salts. In order to solve this general problem the authors analyzed the reaction of the catalytic oxidation of hydrocarbons, and studied each single stage. In the present paper one of the most important reaction stages of the catalytic reaction is studied, i. e., the reaction of a hydroperoxide with a metal salt whose metal has a variable valence. The kinetics of the catalytic decomposition of ethyl benzene hydroperoxide was investigated. The initial decomposition rate is proportional to the concentration of the catalyst (of copper stearate and hydroperoxide). At a high hydroperoxide excess, the catalyst is converted to the inactive form of monovalent copper during the reaction, which is stopped. The amount of decomposed hydroperoxide increases with increasing concentration of the catalyst and of hydroperoxide, as well as with rising temperature. Decomposition mainly proceeds according to the catalytic mechanism; the chain mechanism is of minor importance. When the reaction was carried out in the presence of an inhibitor (diphenyl picryl hydrazyl) it was found that the rate constant of the inhibitor consumption considerably exceeds that of the catalytic decomposition of the hydroperoxide. The diphenyl picryl hydrazyl was synthesized in the Institut organicheskoy khimii AN SSSR

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S/062/61/000/005/002/009  
B118/B208

Catalytic decomposition of...

(Institute of Organic Chemistry, AS USSR). The ethyl benzene hydroperoxide was obtained according to K. I. Ivanov (Ref. 5: Promezhutochnyye produkty i promezhutochnyye reaktsii avtookisleniya uglevodorodov (Intermediate products and intermediate reactions of hydrocarbon autooxidation) Gostoptekhizdat, 1949). There are 9 figures and 8 references: 6 Soviet-bloc and 2 non-Soviet-bloc. The 2 references to English-language publications read as follows: E. A. Braude, A. G. Brook, R. P. Linstead, J. Chem. Soc. 1954, 3574; C.E.H. Bawn, S. T. Mellish, Trans. Faraday Soc. 47, 1216 (1951).

ASSOCIATION: Institut khimicheskoy fiziki Akademii nauk SSSR (Institute of Chemical Physics of the Academy of Sciences USSR)

SUBMITTED: April 4, 1960

Card 3/3

ZAKHAROV, I.V.; SHLYAPINTOKH, V. Ya.

Chemiluminescence in the decomposition of diphenylethane hydro-  
peroxide, and its relation to the kinetics of this process.  
Kin. i kat. 2 no.2:165-171 Mr-Ap '61. (MIRA 14:6)

1. Moskovskiy fiziko-tekhnicheskoy institut, kafedra khimicheskoy  
kinetiki i goreninya. (Ethane) (Luminescence)

28654

S/020/61/139/006/021/022

B103/B101

11.1510

5.5450

AUTHORS: Lebedev, Ya. S., Tsepalov, V. F., and Shlyapintokh, V. Ya.

TITLE: The possibility of using the method of electron paramagnetic resonance to record the active centers in the oxidation of hydrocarbons in the liquid phase

PERIODICAL: Akademiya nauk SSSR. Doklady, v. 139, no. 6, 1961, 1409-1412

TEXT: The authors studied the applicability of electron paramagnetic resonance (epr): a) for determining free radicals; b) for measuring the steady concentration of these radicals in the oxidation of hydrocarbons. A continuation of these studies will probably contribute to the knowledge of the kinetics of processes of other types. From the measured values it is possible to determine directly the rate constants of the elementary reactions that constitute parts of the entire process. Since the concentration of the radicals is low, their determination under steady conditions is difficult. For this reason the active radicals could not be identified during the oxidation of hydrocarbons in the liquid phase. 2 types of active centers take part in the oxidation of hydrocarbons:

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28651  
S/020/61/139/006/021/022  
B103/B101

The possibility of using the method...

hydrocarbon radicals  $\dot{R}$  and peroxide radicals  $\dot{RO}_2$ . At a given initiation rate the steady concentration is known for several substances. It is approximately equal for the following substances: cyclohexene, methyl cyclohexene, 1-octene, dihydromyrcene, ethyl linoleate, digeranyl, tetralin, ethyl benzene, cumene, n-decanal, and benzaldehyde. Under

steady conditions:  $\frac{d(\dot{RO}_2)}{dt} = 0$ , and  $(\dot{RO}_2) = \sqrt{\frac{w_1}{k_6}}$  (1). Hence, the steady

concentration of the  $\dot{RO}_2$ , at a given initiation rate, is the higher the lower the rate constant of  $\dot{RO}_2$  recombination. An increase of the constant to the threefold increases the steady concentration only to the 1.7-fold. In aromatic hydrocarbons, tetralin and ethyl benzene, in which the peroxide group is located at a secondary hydrocarbon atom, the recombination constant is by 1-2 orders of magnitude higher. Among the substances mentioned the cumyl peroxide radicals recombine with the smallest constant. In order to prove the existence of the peroxide radicals their concentration must amount to at least  $1 \cdot 10^{15}$  to  $5 \cdot 10^{15}$  radicals/cm<sup>3</sup>. The authors studied

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The possibility of using the method...

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B103/B101

cumene since they expected the highest concentration in this substance. They used an epr-spectrometer  $MX\Phi-2$  (IKhF-2) with high-frequency modulation of the magnetic field (A. G. Semenov, N. N. Bubnov, PTE, 1, 92 (1959)). During the oxidation, oxygen was continuously bubbled through the hydrocarbon. The following substances were used for the oxidation: I) azobisisobutyronitrile, II) dicyclohexyl percarbonate, III) cobalt stearate, and IV) cobalt acetate. Different initiators give identical spectra. The spectrum is a wide, almost symmetrical singlet ( $\Delta H \approx 18 \pm 2$  oersteds) with a  $g$  factor of  $2.015 \pm 0.001$ . According to the shift of the  $g$  factor and the effective line width, this spectrum is similar to the epr spectrum of the peroxide radicals in the solid phase. In control tests in which isopropyl benzene was replaced by ethyl benzene no epr spectrum was observed in any of the initiators mentioned. Besides, epr absorption disappeared when the oxygen supply was stopped and when nitrogen was blown through for a short period. Ad I) The authors calculated the steady concentrations of the cumyl peroxide radicals at different initiation rates from the known values  $w_i$  and  $k_6$  of Eq. (1). These concentrations were also measured between 70 and 90°C and a

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S/020/61/139/006/021/022  
B103/B101

The possibility of using the method...

concentration of I) between 0.05 and 0.55 mole/l. The absolute values of the concentrations of  $(\dot{R}O_2)_{meas}$  lie between  $2 \cdot 10^{15}$  and  $4 \cdot 10^{16}$  radicals/cm<sup>3</sup>.

The measured steady concentration of  $RO_2$  radicals was close to the calculated one. In experiments with II) the authors measured concentrations of  $4 \cdot 10^{15}$  to  $2 \cdot 10^{16}$  radicals/cm<sup>3</sup>. The rate constant of decay of II) into radicals is unknown. The authors assume that its decay rate is equal to the decay rate into radicals. Thus, they calculate the initiation rate and find that the measured concentrations of the  $RO_2$  radicals are

$1/4$  to  $1/2$  of the calculated values. Since this rate is unknown in experiments with III) and IV) the measured and calculated radical concentrations could not be intercompared. There are 2 figures, 1 table, and 11 references: 4 Soviet and 7 non-Soviet. The four most important references to English-language publications read as follows: Ref. 1: H. W. Melville, S. Richards, J. Chem. Soc. 1954, 944; Ref. 4: H. R. Cooper, H. W. Melville, J. Chem. Soc., 1951, 1993; Ref. 5: L. Bateman, G. Gee, Trans. Farad. Soc. 47, 155 (1951); Ref. 6: T. A. Ingles, H. W. Melville, Proc. Roy. Soc., A218, 163 (1953).

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28654

S/020/61/139/006/021/022  
B103/B101

The possibility of using the method...

ASSOCIATION: Institut khimicheskoy fiziki Akademii nauk SSSR (Institute  
of Chemical Physics of the Academy of Sciences USSR)

PRESENTED: May 20, 1961, by V. N. Kondrat'yev, Academician

SUBMITTED: May 20, 1961

X

Card 5/5

ZAKHAROV, I.V.; SHLYAPINTOKH, V.Ya.

Kinetics of chemiluminescence in the reaction of the thermal  
decomposition of diphenylethane hydroperoxide. Trudy MFTI  
no.8:137-149 '62. (MIRA 15:5)

(Luminescence)  
(Bibenzyl)

S/195/62/003/006/005/011  
E075/E436

AUTHORS: Tsepalov, V.F., Shlyapintokh, V.Ya.

TITLE: Rate constants of elementary reactions in the oxidation of ethylbenzene with molecular oxygen

PERIODICAL: Kinetika i kataliz, v.3, no.6, 1962, 870-876

TEXT: The method of intermittent illumination was used to determine the rate constants for the elementary reactions of chain propagation and stoppage. The rate of oxidation was measured by  $O_2$  absorption in a vacuum apparatus with an automatic pressure regulator. Light was emitted from a Hg lamp, the pulse duration ranging from 0.002 to 10 sec. Anthraquinone ( $1.4 \times 10^{-4}$  mole/litre) was used as a photosensitizer. The reaction vessel was shaken to make the oxidation not dependent on diffusion of  $O_2$ . The oxidation was carried out at 1 atm between 50 and 90°C, the degree of oxidation of ethylbenzene not exceeding 0.5%. The oxidation scheme considered was: chain initiation

(I)  $\dot{R}$  or  $\dot{RO}_2$ , rate of initiation  $W_1$ ; chain propagation

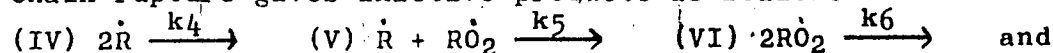
(II)  $\dot{R} + O_2 \xrightarrow{k_2} \dot{RO}_2$  and (III)  $\dot{RO}_2 + RH \xrightarrow{k_3} RO_2H + \dot{R}$ .

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Rate constants ...

S/195/62/003/006/005/011  
E075/E436

Chain rupture gives inactive products as follows:



(VII)  $R\dot{O}_2 + \text{inhibitor} \xrightarrow{k_7} \dots$  The reaction rate applicable to short and long chains is given by

$$\frac{d[O_2]}{dt} = k_3 k_6^{-1/2} W_i^{1/2} [RH] + \frac{1}{2} W_i \quad (3)$$

$W_i$  was determined by inhibiting the reaction with  $\alpha$ -naphthol. As  $(d[O_2])/dt$  varied linearly with the reciprocal of the inhibitor concentration ( $1/[B]$ ) the values of  $W_i$  were determined graphically by extrapolating  $1/[B]$  to zero. The values of

$k_3 \times k_6^{-1/2}$  were determined by three independent methods (inhibition with  $\alpha$ -naphthol, inhibition with azo-bis-isobutyronitrile, oxidation in the presence of cobalt acetate catalyst) and ranged from 4.00 at 50°C to 22.2 (1 mole x sec)<sup>1/2</sup> x 10<sup>-4</sup> at 100°C. The agreement between the values determined by the three

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Rate constants ...

S/195/62/003/006/005/011  
E075/E436

methods indicated that in the photosensitized oxidation of  $O_2$  radicals did not take part in chain rupture, the rupture occurring via peroxide radicals. The mean life of radicals  $\dot{R}O_2$  is given by

$$\tau = \frac{[\dot{R}O_2]}{k_6 [\dot{R}O_2]^2} = \frac{1}{k_6 [\dot{R}O_2]^{1/2}} \quad \text{and} \quad \tau = k^{-1/2} W_i^{-1/2} \quad (4)$$

The quantity  $\tau \times W_i$  did not change with temperature, which indicated that the activation temperature of the radical recombination is zero. The mean value of  $k_6$  was  $3.2 \times 10^{-4} \text{ cm}^3/\text{sec}$ . From this value the constant  $k_7$  for the chain propagation was found to be  $1.6 \times 10^{-15} e^{-8500/RT} \text{ cm}^3/\text{sec}$ .

The constant  $k_7$  was calculated using the equation

$$\frac{d[O_2]}{dt} = W_i \left( 1 + \frac{k_3 [RH]}{k_7 [B]} \right) \quad (5)$$

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Rate constants ...

S/195/62/003/006/005/011  
E075/E436

For the inhibition by  $\alpha$ -naphthol,

$$k_7 = 1.7 \times 10^{-12} e^{-6800/RT} \frac{\text{cm}^3}{\text{sec}}$$

There are 3 figures and 2 tables.

ASSOCIATION: Institut khimicheskoy fiziki AN SSSR  
(Institute of Chemical Physics AS USSR)

SUBMITTED: October 31, 1961

Card 4/4

s/658/62/000/010/008/008  
A059/A126

**AUTHORS:** Zakharov, I.V., Shlyapintokh, V.Ya., Candidate of Chemical Sciences

**TITLE:** Kinetics of chemoluminescence in the reaction of catalyzed oxidation of ethylbenzene

**SOURCE:** Moscow. Fiziko-tekhnicheskiy institut. Trudy, no. 10, 1962. Issledovaniya po fizike i radiotekhnike. 111 - 118

**TEXT:** The assumption that oxidation as a chain reaction taking place with the participation of free radicals should be accompanied by luminescence is experimentally demonstrated on the example of ethylbenzene oxidation catalyzed by cobalt acetate, the kinetics of which has been described before. Oxidation was performed in a special constant-temperature vessel, with the photomultiplier Ф9У-18 (FEU-18) placed behind it. In the course of the experiment, air was passed, which had been dried with CaCl<sub>2</sub>. Glacial acetic acid was used as the inert solvent. Chemoluminescence was measured at temperatures between 50 and 98°C with catalyst concentrations between 0 and 20 · 10<sup>-3</sup> moles/l, and ethylbenzene concentrations between 5 and 40% by volume. Luminescence is recorded only in the

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Kinetics of chemoluminescence in the reaction of ....

S/658/62/000/010/008/008  
A059/A126

presence of oxygen, which shows that the chemoluminescence observed is due only to oxidation. After some time, which increases with increasing catalyst concentration, steady luminescence intensity is established, which shows a maximum. A linear relation between chemoluminescence intensity and oxidation rate is found. The introduction of hydroperoxide leads to the disappearance of the initial stage of growth of luminescence intensity, which increases with increasing concentration of the hydroperoxide added. The development of luminescence in time is related to the accumulation of hydroperoxide in the system, and the steady luminescence intensity corresponds to steady oxidation, in which the decay velocity of hydroperoxide is constant. The intensity was found to be proportional to the square of ethylbenzene concentration. As a result, chemoluminescence in the reaction studied is assumed to be excited by the energy set free in peroxide-radical recombination, which is the only exothermic stage in oxidation. This energy which is in excess of 50 - 60 kcal/mole is sufficient to excite luminescence in the visible part of the spectrum in the sensitivity range of the photomultiplier used. As a result of kinetic studies, it is found that the rate of hydroperoxide decay is, at all catalyst concentrations, proportional to the concentration of the nondecomposed hydroperoxide,

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Kinetics of chemoluminescence in the reaction of .... S/658/62/000/010/008/008  
A059/A126

$$-\frac{d(P)}{dt} = k_{\text{eff}}(P), \quad (4)$$

and that the luminescent intensity is proportional to the rate of catalytic decay of the hydroperoxide,

$$I \sim \frac{d(P)}{dt}, \quad (5)$$

where  $k_{\text{eff}}$  is the constant of effective decay depending on the catalyst concentration. There are 8 figures.

Card 3/3

POSTNIKOV, L.M.; ZILYAPINTORR, V.Ya.; SHUVALOV, V.F.

Chemiluminescence in the gaseous oxidation of acetaldehyde.  
Zhur.fiz.khim. 36 no.10:2284-2286 O '62. (MIRA 17:4)

1. Institut khimicheskoy fiziki AN SSSR.

S/062/63/000/002/006/020  
B144/B186

AUTHORS: Kulitski, Z. I., Terman, L. M., Tsepalov, V. F., and Shlyapintokh, V. Ya.

TITLE: Determination of the rate constants of initiator decomposition and of the initiation efficiency

PERIODICAL: Akademiya nauk SSSR. Izvestiya. Otdeleniye khimicheskikh nauk, no. 2, 1963, 253 - 257

TEXT: The rate constants of initiator decomposition can be determined from the relation between oxidation rate and concentration. The oxidation rates of cumol and ethyl benzene containing iso-bis-isobutyro nitrile (I) and di-cyclohexyl peroxy dicarbonate (II) as initiators were studied at 60 - 90°C in an apparatus described previously (Kinetika i Kataliz (1962), no. 6). The O<sub>2</sub> absorption-versus-time curves showed that the oxidation rate is constant at low temperatures, where the initiator concentration remains constant, but decreases at higher temperatures owing to initiator decomposition. The order of the initiation reaction was determined using the equation.

$$-d(O_2)/dt = k_3 k_6^{-1/2} (RH)(e \cdot k_{eff})^{1/2} \cdot (Y)^{n/2} \quad (3) \text{ for the rate of } O_2 \text{ absorption,}$$

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S/062/63/000/002/006/020  
B744/B186

Determination of the rate...

where RH is the substance to be oxidized,  $e$  the initiation efficiency,  $k_{\text{eff}}$  the effective rate constant of initiator decomposition,  $Y$  the initiator, and  $n$  the order of the initiation reaction. If

$(Y) = (Y)_0 e^{-k_{\text{eff}} t}$  is introduced into (3) under the assumption of a first-order reaction for the decomposition of the initiator,  $\log(-d(O_2)/dt) - \log(-d(O_2)/dt)_0 - k_{\text{eff}} t/4.6$  is obtained, where  $(-d(O_2)/dt)_0$  is the initial reaction rate and  $Y_0$  the initial concentration of the initiator. Plotting curves for the time dependence of  $\log(d(O_2)/dt)/(d(O_2)/dt)_0$  established that both initiators decompose in a first-order reaction. The rate constants of initiator decomposition,  $k_{\text{eff}}$ , were calculated from this graph.

The activation energies were 29.6 kcal/M for II, and 31.2 kcal/M for I. The decomposition rate constants were  $2.71 \cdot 10^{15} e^{-29600/RT}$  for II, and  $2.63 \cdot 10^{15} e^{-31200/RT}$  for I. The initiation efficiency was calculated from the initiation rate and the rate of initiator decomposition. The values

Card 2/3

Determination of the rate...

S/062/63/000/002/006/020  
B144/B186

obtained were 1.1 for I and 1.4 for II. There are 5 figures and 2 tables.

ASSOCIATION: Institut khimicheskoy fiziki Akademii nauk SSSR (Institute  
of Chemical Physics of the Academy of Sciences USSR)

SUBMITTED: May 14, 1962

Card 3/3



KARPUKHIN, O.N.; RUSINA, I.F.; NIKIFOROV, G.A.; SHLYAPINTOKH, V.Ya.

Sterically hindered phenolphthaleins and the possibility of  
using them for the study of inhibited oxidation processes.  
Neftekhimii 3 no.4:579-583 J1-Ag '63. (MIRA 16:11)

1. Institut khimicheskoy fiziki AN SSSR.

L 10593-63

RM/WW

EWP(j)/EPF(c)/EWT(l)/EWT(m)/BDS AFFTC/ASD Pc-l/Pr-l

ACCESSION NR: AP3001487

S/0195/63/004/002/0239/0243

70  
68

AUTHOR: Zakharov, I. V.; Shlyapintokh, V. Ya.

TITLE: Chemiluminescence in slow chemical reactions. 1. The mechanism governing chemiluminescence in the catalyzed reaction of ethylbenzene oxidation

SOURCE: Kinetika i kataliz, v. 4, no. 2, 1963, 239-243

TOPIC TAGS: chemiluminescence in oxidation benzene, cobalt acetate, hydroperoxide

ABSTRACT: Chemiluminescence was observed during the oxidation of ethylbenzene in a reaction catalyzed with cobalt acetate. Its intensity is proportional to the rate of reaction and it changes with the temperature, concentration of the catalyst, concentration of the hydrocarbon, and the rate of oxidation. The proposed kinetics explains the principal mechanism governing chemiluminescence. The experiment confirms the assumption of chemiluminescence in reactions and decompositions of hydroperoxides by using the ordinary salt catalysts. The discovered proportionality between the intensity of glow and the rate of chemical conversion can be utilized in the investigation of kinetics and also for the control and direction of the process of catalyzed oxidation. Orig. art. has:

Card 1/2

*Instit. of Chem. Physics*

VASIL'YEV, R.F.; VICHUTINSKIY, A.A.; KARPUKHIN, O.N.; SHLYAPINTOKH, V.Ya.

Chemiluminescence in slow chemical reactions. Part 2: Effect of the chemical composition of the system on chemiluminescence intensity. Kin. i kat. 4 no.3:382-387 My-Je '63.

(MIRA 16:7)

1. Institut khimicheskoy fiziki AN SSSR.  
(Luminescence) (Chemical reaction, Rate of)

ZAKHAROV, I.V.; SHLYAPINTOKH, V.Ya.

Chemiluminescence in slow chemical reactions. Part 3:  
Chemiluminescent method used for studying the kinetics of  
hydroperoxide accumulation in the reaction of catalyzed oxidation  
of ethylbenzene. Kin.i kat. 4 no.5:706-712 S-0 '63.  
(MIRA 16:12)

1. Moskovskiy fiziko-tekhicheskiy institut i Institut  
khimicheskoy fiziki AN SSSR.

KARPUKHIN, O.N.; SHLYAPINTOKH, V.Ya.; ZOLOTOVA, N.V.

Chemiluminescence in the reactions of inhibited oxidation and the activity of inhibitors. Report No.1: Theory of chemiluminescent methods for determining the activity of inhibitors. Izv. AN SSSR Ser.khim. no.10:1718-1721 0 '63.

Chemiluminescence in the reactions of inhibited oxidation and the activity of inhibitors. Report No.2: Measurement of the activity of inhibitors by the chemiluminescent methods. 1722-1727

(MIRA 17:3)

1. Institut khimicheskoy fiziki AN SSSR.

KARPUKHIN, O.N.; SHLYAPINTOKH, V.Ya.; RUSINA, I.F.; ZOLOTOVA, N.V.

Chemiluminescent method for determining the inhibitors of free radical reactions. Zhur.anal.khim. 18 no.8:1021-1025 Ag '63.  
(MIRA 16:12)

1. Institute of Chemical Physics, Academy of Sciences, U.S.S.R., Moscow.

L 9865-63 EPF(c)/EWT(1)/EWT(m)/BDS--AFFTC/ASD--Pr-4--RM/WW/MAY/IJP(C)  
ACCESSION NR: AP3001349 S/0048/63/027/006/0735/0738

AUTHOR: Postnikov, L. M.; Shuvalov, V. F.; Shlyapintokh, V. Ya. 66 1  
65

TITLE: Nature of chemiluminescence associated with low-temperature oxidation of acetaldehyde [Report of the Eleventh Conference on Luminescence held in Minsk from 10 to 15 September 1962]

SOURCE: AN SSSR. Izv. Seriya fizicheskaya, v. 27, no. 6, 1963, 735-738

TOPIC TAGS: chemiluminescence, vapor phase reactions, reaction kinetics, acetaldehyde

ABSTRACT: Chemiluminescence<sup>γ</sup> - luminescence accompanying chemical reactions - has been under study at the Institute of Chemical Physics of the Academy of Sciences SSSR for several years, and it has been established that the emission appears as a result of radical recombination. Most of the previous studies, however, were concerned with reactions in the liquid phase. Accordingly, it was deemed of interest to investigate reactions in the vapor phase. Chemiluminescence has been observed (in some cases for the first time) incident to decomposition of methyl

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L 9865-63

ACCESSION NR: AP3001349

hydroperoxide, oxidational decomposition of deuterio butyl peroxide and azomethane, slow oxidation of n-butane, ethyl ether, acetaldehyde, etc. The present experiments were carried out in a 550 cc molybdenum glass reaction vessel at temperatures from 100 to 200°C and initial pressures from tens to hundreds mm Hg. The variations in chemiluminescence and pressure were recorded automatically; when indicated, the end products were subjected to chemical analysis. The time variation of the chemiluminescence incident to oxidation of acetaldehyde proved to be distinctive; most curves exhibit two peaks; one sharp, the other flat (the time curves and spectra for oxidation of acetaldehyde are reproduced). This indicates that the reaction proceeds in two stages. Hence observation of chemiluminescence provides a means for studying the kinetics of some chemical reactions. Orig. art. has: 3 figures.

ASSOCIATION: Institut khimicheskoy fiziki Akademii nauk SSSR (Institute of Chemical Physics, Academy of Sciences, SSSR)

SUBMITTED: 00

DATE AQ: 01Jul63

ENCL: 00

SUB CODE: PH, CH

NR REF SOV: 006

OTHER: 006

Card 2/2 *ja/mk*



KARPUKHIN, O.N.; SHLYAPINTCKH, V.Ya.; ZOLOTOVA, N.V.; KOZLOVA, Z.G.; RUSINA, I.F.

Mechanism of the weakening of chemiluminescence by inhibitors of free radical reactions. Zhur.fiz.khim. 37 no.7:1636-1638 J1 '63.

(MIRA 17:2)

1. Institut khimicheskoy fiziki AN SSSR.

SHLYAPINTOKH, V.Ya.; POSTNIKOV, L.M.; KARPUKHIN, O.N.; VERETIL'NIYY, A.Ya.

Chemiluminescence during alternating current electrolysis. Zhur.fiz.  
khim. 37 no.10:2374-2375 O '63. (MIRA 17:2)

45160

S/020/63/148/002/037/037  
B124/B186

5470  
AUTHORS:

Shuvalov, V. F., Vasil'yev, R. F., Postnikov, L. M.,  
Shlyapintokh, V. Ya.

TITLE:

Formation of excited formaldehyde molecules in low-temperature  
oxidation of acetaldehyde

PERIODICAL:

Akademiya nauk SSSR. Doklady, v. 148, no. 2, 1963, 388-390

TEXT: The project consisted in determining the chemical nature of the  
luminescent particles in the oxidation of acetaldehyde. It is proved that  
in this reaction the luminescence is connected with the formation of ex-  
cited formaldehyde molecules. Chemi-luminescence in reactions which pro-  
ceed under formation of alkoxy radicals is also explained in this way. The  
luminescent particles in the slow oxidation of acetaldehyde in the gas phase  
are identified experimentally by taking the chemi-luminescence spectra with  
a high-power spectrometer developed by R. F. Vasil'yev, S. M. Petukhov and  
T. N. Zhuchkova; the instrument is described in ZhFKh, v. 36, No. 10, 2284  
(1962). The chemi-luminescence spectrum of a mixture of 50 mm Hg acetalde-  
hyde and 47 mm Hg oxygen was taken at 182°C, chemi-luminescence having a  
maximum value. The kinetic curve of chemi-luminescence has two peaks. In  
Card 1/3

Formation of excited formaldehyde...

S/020/63/148/002/037/037  
B124/B186

the section following the second peak the intensity of luminescence changes but little with time. It has been found that the spectrum taken in this section practically coincides with the fluorescence spectrum of formaldehyde. The formation of formaldehyde in the reaction products is proved also by chemical analysis. With the aid of light filters it was shown that between 180 and 120°C the position of the luminescence maximum and the total shape of the spectrum do not change. Hence it can be concluded that also at temperatures below 180°C the second luminescence maximum is related to the formation of formaldehyde. The kinetic curves of luminescence at 182°C and with a composition of the mixture of 50 mm Hg CH<sub>3</sub>CHO and 35 mm Hg O<sub>2</sub> were taken at 370, 425, and 510 mμ. It was found that the intensity ratio remains practically constant. This proves that also in the region of the first peak, luminescence is connected with excited formaldehyde molecules. This example shows that the reactions necessary for the formation of excited formaldehyde molecules take place not only in cool flames but even at much lower temperatures. There are 3 figures.

ASSOCIATION: Institut khimicheskoy fiziki Akademii nauk SSSR (Institute of Chemical Physics of the Academy of Sciences USSR)

Card 2/3

Formation of excited formaldehyde...

S/020/63/148/002/037/037  
B124/B186

PRESENTED: June 11, 1962, by V. N. Kondrat'yev, Academician

SUBMITTED: July 10, 1962

f

Card 3/3

POSTNIKOV, L.M.; SHLYAPINTOKH, V.Ya.

Mechanism of the formation of excited formaldehyde molecules in  
oxidation reactions. Dokl. AN SSSR 150 no.2:340-342 My '63.  
(MIRA 16:5)

1. Institut khimicheskoy fiziki AN SSSR. Predstavleno akademikom  
V.N.Kondrat'yevym.  
(Formaldehyde) (Oxidation) (Reaction, Rate of)

L 12629-63 EWP(j)/EPF(c)/EWP(q)/EWT(m)/BDS AFFTC/ASD Pe-4/Pr-4

RM/WN/JD

ACCESSION NR: AP3002878

S/0020/63/150/005/1069/1072

68  
67

AUTHOR: Zakharov, I. V.; Shlyapintokh, V. Ya.

TITLE: Chemiluminescence and reaction mechanism of the catalyzed decomposition of ethylbenzene hydroperoxide

1

SOURCE: AN SSSR. Doklady\*, v 150, no. 5, 1963, 1069-1072

TOPIC TAGS: chemiluminescence, cobalt acetate, trivalent cobalt

ABSTRACT: This study is a continuation of the work previously done on the law of chemiluminescence in the oxidation of ethylbenzene using cobalt acetate as a metal salt catalyst with a variable valence. The chemiluminescence in this reaction depends on the recombination of peroxide radicals formed as a result of the catalyzed decomposition of hydroperoxide. The intensity of chemiluminescence is proportional to the speed of decomposition. The value obtained from the light intensity curves and from the analysis of hydroperoxide decomposition are in agreement. This gives a possibility of utilization of chemiluminescence method for the investigation of the kinetics of catalyzed hydroperoxide decomposition. It was found that the higher the concentration of catalyst, the higher is the maximum intensity of the chemiluminescence. The rate of decomposition is doubled

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L 12629-63

ACCESSION NR: AP3002878

when the rate of consumption of trivalent cobalt becomes equal to its rate of formation. The proposed catalytic de composition is realized in the reactions in which the salts of di- and trivalent cobalt take place interchangeably. Orig. art. has: 1 table and 4 figures.

ASSOCIATION: Institut khimicheskoy fiziki Akademii nauk SSSR (Institute of Chemical Physics, Academy of Sciences SSSR)

SUBMITTED: 01Feb63

DATE ACQ: 15Jul63

ENCL: 00

SUB CODE: 00

NO REF SOV: 005

OTHER: 000

*mcs/ss*

Card 2/2



ACCESSION NR: AP4016517

S/0195/64/005/001/0064/0070

AUTHOR: Lebedev, Ya. S.; Tsepalov, V. F.; Shlyapintokh, V. Ya.

TITLE: Measuring the stationary peroxide radical concentration in the cumene oxidation reaction by the EPR method

SOURCE: Kinetika i kataliz, v. 5, no. 1, 1964, 64-70

TOPIC TAGS: peroxide radical, concentration determination, cumene oxidation, peroxide radical formation, liquid phase oxidation, recombination rate, cobalt stearate catalyst, azobisisobutyronitrile, dicyclohexylpercarbonate, EPR analysis, cumyl peroxide

ABSTRACT: A study of the liquid phase oxidation of hydrocarbons showed that the peroxide radical recombination rate constant is approximately the same for olefinic materials, and 1-2 orders higher for aromatic hydrocarbons. Cumyl peroxide was selected for further study since it has the smallest recombination rate constant. The oxidation of cumene was then effected in the resonator

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ACCESSION NR: AP4016517

of the EPR spectrometer. The reaction was catalyzed with cobalt stearate or initiated with azobisisobutyronitrile or with dicyclohexylpercarbonate. In changing the concentration of the latter from 0.02-0.55 mol./l., at 68-90C, the initiation rate changed by a factor of 50, from  $5 \times 10^{-6}$  to  $2.4 \times 10^{-4}$  mol/l·sec. The EPR spectra, determined by the cumyl peroxide radicals, are identical, although oxidation was initiated by different radicals. The peroxide radical concentration measured in this work essentially approaches the values calculated from the known rate of initiation and the recombination rate constant. The slightly lower measured values are explained as due to experimental errors such as insufficient O<sub>2</sub>, incorrect placement of the ampoule in the resonator, etc. Orig. art. has: 2 figures, 4 equations, 1 formula

ASSOCIATION: Institut khimicheskoy fiziki AN SSSR (Institute of Chemical Physics AN SSSR)

SUBMITTED: 26Apr62

DATE ACQ: 18Mar64

ENCL: 00

SUB CODE: CH, PH

NO REF SOV: 007

OTHER: 013

Card 2/2

KOZLOVA, Z.G.; TSEPALOV, V.F.; SHLYAPINTOKH, V.Ya.

Mechanism of hydrocarbon oxidation catalyzed by cobalt salts.

Kin. i kat. 5 no.5:868-876 S-0 '64.

(MIRA 17:12)

1. Institut khimicheskoy fiziki AN SSSR.

TSEPALOV, V.F.; SHLYAPINTOKH, V.Ya.; CHZHOU PEY-KHUAN [Chou P'ei-huang]

Kinetics of cooxidation of cumene and ethylbenzene. Part 1.  
Zhur. fiz. khim. 38 no.1:52-58 Ja'64. (MIRA 17:2)

1. Institut khimicheskoy fiziki AN SSSR.

L 27269-65 EWT(m)/EPF(c)/EWP(j)/T Pc-4/Pr-4 RPL BW/WH/JFW/JWD/RM

ACCESSION NR: AP4011449 S/0076/64/038/001/0156/0160

AUTHOR: Karpukhin, O. N. (Moscow); Shlyapintokh, V. Ya. (Moscow);  
Mikhaylov, I. D. (Moscow)

TITLE: Chemiluminescence and the rate of the elementary reaction in the  
co-oxidation of cumene and ethylbenzene.

SOURCE: Zhurnal fiz. khim. v. 38, no. 1, 1964, 156-160

TOPIC TAGS: chemiluminescence, oxidation kinetics, cumene oxidation  
kinetics, ethylbenzene oxidation kinetics, peroxide radical recombination

ABSTRACT: The dependence of the chemiluminescence intensity upon the  
mixture composition in the azobisisobutyronitrile-initiated co-oxidation of  
cumene and ethylbenzene was investigated. The system contains two kinds of  
active radicals whose recombination excites chemiluminescence. The relative  
contribution of each radical is shown in Figure 1, the change in intensity in  
relation to composition in Figure 2. Chemiluminescence intensity quantitative-

Card 1/3

34  
26 B

L 27269-65

ACCESSION NR: AP4011449

2

ly characterized the relative reaction rates of recombination of the cumene and ethylbenzene radicals. ( Orig. art. has: 3 figures and 4 equations.

ASSOCIATION: Institut khimicheskoy fiziki AN SSSR (Institute of Chemical Physics, AN SSSR)

SUBMITTED: 25Apr63

ENCL: 02

SUB CODE: GC, OP NO REF SOV: 010

OTHER: 001

Card 2/4

27269-65

ACCESSION NR: AP4011449

ENCLOSURE: 01

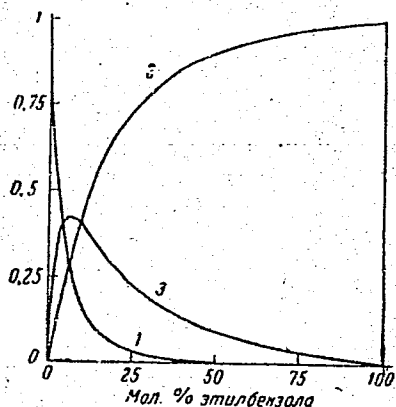


Figure 1. Relative contribution of the individual recombination reactions of the peroxide radicals to the total recombination rate in mixtures of cumene and ethylbenzene, depending on composition of the mixture at 60C. 1. recombination rate of cumene peroxide radicals. 2. recombination rate of ethylbenzene peroxide radicals. 3. recombination rate of cumene and ethylbenzene peroxide radicals

Cum  
3/4

ACCESSION NR: AP4019518

S/0076/64/038/002/0351/0355

AUTHORS: Tsepalov, V.F. (Moscow); Shlyapintokh, V.Ya. (Moscow);  
Chou, P'ei-huang (Moscow)

TITLE: Kinetics of cooxidation of cumene and ethylbenzene II. Determination of rate constants of cross reactions of chain extensions and rupture.

SOURCE: Zhurnal fizicheskoy khimii, v.38, no.2, 1964, 351-355

TOPIC TAGS: cumene ethylbenzene cooxidation, ethylbenzene peroxide, cumene peroxide, cumene, benzene

ABSTRACT: This is a continuation of the work by the same authors (Zh.F.Kh., 38, 1964) covering the kinetics of cooxidation of the same compounds at 60 and 80C. The purpose of the present work is to correct data concerning the rate constant of recombination of peroxide radicals of cumene as given by H. Melville, S. Richards (J.Chem.Soc. 944, 1954) which were based on an erroneous assumption on the initiation of two chains. The kinetic regularities observed in the cooxidation of cumene and ethylbenzene are qualitatively interpreted. Values

Card 1/2



CHIVALOV, V.F.; LEHEDEV, Ya.S.; TSEPALOV, V.F.; SHLYAPINTOKH, V.Ya.

Electron paramagnetic resonance spectra of peroxide radicals  
in the liquid phase. Zhur. fiz. khim. 38 no.5:1287 My '64.  
(MIRA 18:12)

1. Institut khimicheskoy fiziki AN SSSR. Submitted March  
28, 1963.

L 26657-65 EWG(j)/EWT(l)/EWT(m)/EPF(c)/EWA(d)/EPR/EWP(j)/EEG(t)/EWP(t)/EWP(b)  
Pc-l/Pr-l/Ps-l/Pad/Feb IJP(c)/RPL RM/WW/JFW/JD/HW/WB/GS  
ACCESSION NR: AT5002264 S/0000/64/000/000/0190/0195

57  
45  
B+1

AUTHOR: Lebedev, Ya. S.; Tsepalov, V. F.; Shlyapintokh, V. Ya.

TITLE: Use of electron paramagnetic resonance for the study of active centers in liquid-phase oxidation reactions

SOURCE: Soveshchaniye po fizicheskim metodam issledovaniya stroyeniya molekul organicheskikh soyedineniy i khimicheskikh protsessov. Frunze, 1962. Trudy. Frunze, Izd-vo Ilim, 1964, 190-195

TOPIC TAGS: electron paramagnetic resonance, liquid phase oxidation, active center, EPR spectrum, peroxide radical, cumene oxidation

ABSTRACT: This investigation was undertaken to determine the steady concentrations of peroxide radicals in liquid-phase oxidation reactions by means of EPR spectra. Experiments were conducted on an IKhF-2 spectrometer with a high-frequency modulation field. The instrument recorded the first derivative of the EPR line of the peroxide radical, simultaneously with the signal from the standard sample (carbon). The reaction was conducted directly in an EPR resonator of the spectrometer. For this purpose, an ampule of cumene was placed in the resonator and heated with a stream of hot air. Oxidation was catalyzed by cobalt stearate or, initiated by azodiisobutyronitrile (I) or dicyclohexylpercarbonate (II).

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L 26657-65

ACCESSION NR: AT5002264

3

Temperature was measured with a thermocouple immersed in the ampule. Oxygen was bubbled through the sample. Free radicals were observed and identified, from their spectra, as cumene peroxide radicals. Experiments on the measurement of the steady-state concentration of cumene peroxide radicals were conducted at 68-90C and with concentrations of I of 0.02-0.55 mole/liter. Initiation speeds varied from  $5 \times 10^{-6}$  to  $2.4 \times 10^{-4}$  mole/liter, sec. With I, the speed was calculated from  $w_i = 1.2 \times 1.58 \times 10^{15} \cdot e^{-30800/RT}$ . Absolute values of the experimental concentrations of peroxide radicals lay within  $5 \times 10^{15}$  --  $4 \times 10^{16}$  radicals/cm<sup>3</sup>. Calculated and measured values were close. Orig. art. has: 1 table, 2 figures and 3 formulas.

ASSOCIATION: Institut khimicheskoy fiziki AN SSSR (Chemical physics institute, AN SSSR)

SUBMITTED: 19Jun64

ENCL: 00

SUB CODE: GC, NP

NO REF SOV: 005

OTHER: 011

Card 2/2

1c

L 34143-65 EWT(1)/EWT(m)/ENG(m)/T IJR(c) RWH/GS  
ACCESSION NR: AT5006090 S/0000/64/000/000/0137/0145

24  
210  
P1

AUTHOR: Vasil'yev, R.F.; Vichutinskiy, A.A.; Zakharov, I. V.; Karpukhin, O. N.;  
Postnikov, L. G.; Shlyapintokh, V. Ya.

TITLE: Chemiluminescence in the study of the kinetics and mechanism of chemical  
reactions of organic compounds

SOURCE: Soveshchaniye po fizicheskim metodam issledovaniya organicheskikh sove-  
dineniy i khimicheskikh protsessov. Frunze, 1962. Trudy. Frunze, Izd-vo Ilim,  
1964, 137-145

TOPIC TAGS: reaction kinetics, organic mechanism, chemiluminescence, radical re-  
combination, luminescence spectrum, hydrocarbon oxidation, hydroperoxide decompo-  
sition

ABSTRACT: The article deals with the chemiluminescence, produced by recombination  
in radical reactions. Measurement of the intensity of chemiluminescence at var-  
ious temperatures provides a rapid method for determining the initiation rate or  
the activation energy of decomposition of the initiator of the reaction. The tem-  
perature dependence of the intensity of chemiluminescence in the course of oxida-  
tion of various hydrocarbons initiated by different hydroperoxides is discussed.

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